PHYSICS OF NON-DESTRUCTIVE TESTING

with particular reference to some of the new aspects

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Foreword

THE contributions published in this Supplement are selected from those presented during the past few months at meetings of the Non-Destructive Testing Group of The Institute of Physics. They include most of those read at the Conference held in Bristol in July, 1956, and are printed here in the order in which they were presented.

The purpose of presenting this collection is to enable engineers, metallurgists and indeed all those concerned with non-destructive testing, to appreciate the importance of the new methods which are resulting from applications of physics to this field and to give them an opportunity of considering how far further suggestions for utilizing the physical behaviour of substances under various conditions can be used and developed as methods for non-destructive testing.

J. THEWLIS

Chairman, Non-Destructive Testing Group

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Some aspects of the mechanical testing of non-metallic solids

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Some problems associated with the mechanical testing of several classes of non-metals are reviewed. The difficulties encountered in measuring the elastic properties of rubbers, plastics and fibrous materials are considered and tests on the mechanical strength of glass-like materials are discussed. The significance of static and dynamic hardness measurements on non-metals is then considered in detail and the way in which such quantities as rebound hardness may depend on the conditions of test rather than on the properties of the material being investigated is described.

INTRODUCTION

The mechanical testing of non-metallic solids is an extremely wide subject and it is impossible in a short paper to do more than indicate some of the problems involved. The present paper discusses those few aspects with which the author has personally become familiar rather than attempting, for example, to summarize the 6000 pages which the current *Standard Specifications of the American Society for Testing Materials* devotes to this subject.

The ultimate aim in carrying out a mechanical test on a sample is to ensure that the material will withstand the stresses to which it is subjected in use without fracturing or seriously changing its shape. The tests themselves may, however, be carried out at a number of different levels, depending on the more immediate aim of the investigator. Sometimes, however, the product in its final form is tested by being subjected to the type of treatment which it is likely to receive; for example, a test which has been used by a firm of telephone manufacturers is to drop their instruments on to a hard floor from various heights and see whether or not they break. There is much to be said for this type of test, but it is clearly neither desirable nor even feasible always to adopt such a direct method of approach, and most mechanical tests involve making measurements under one set of conditions in order to find out what will occur under an entirely different set of conditions. This necessarily requires a knowledge of how the material behaves under various types of loading and consequently depends on a theory of its mechanical behaviour. It is here that the mechanical testing of non-metals leads to special difficulties in that, whilst the behaviour of metals in their elastic and plastic states has been investigated very thoroughly, and a large reserve of both empirical and theoretical knowledge has been accumulated in the subject known to engineers as "strength of materials," the mechanical behaviour of non-metals, which is very much more complex, has until recently received comparatively little attention.

Where all that is required from the test is to ensure that a batch of exactly similar specimens of a single material have approximately the same mechanical properties, many types of test are adequate, in that so long as the parameters measured are related, however remotely, to the parameters in which the investigator is interested, the test may be a workable one. An extreme example may perhaps be taken from the culinary arts, where the shade of brown of the top surface of a cake can be taken as an indication of the taste and texture of the interior. That this is not an infallible test must be well known to most who have attempted to practise the art as well as to many innocent victims.

The more removed the measured parameters in a test are from those which are really relevant, the greater is the possibility of error in applying such tests to materials for which there is no body of accumulated experience. Even when the physical measurements appear to be closely related to the properties which it is required to investigate, misleading results may sometimes be obtained from a failure to appreciate the exact significance of the test. Later in this paper some investigations by the author and his colleagues on the nature of dynamic and static hardness will be described to illustrate this point.

A more general approach to testing is that in which the relations between the measured physical properties of the material are correlated with its microscopic or chemical constitution. Whilst work of this kind, in so far as it is carried out at all, tends to be confined to the research laboratory rather than to the testing laboratory, in the view of the author it is only this more fundamental approach which can lead to a better understanding of the significance of physical tests and thus to an improvement of products as opposed to a mere sorting of them into those which conform to an often arbitrarily chosen standard and those which do not.

CLASSES OF NON-METALLIC SOLIDS

The different types of non-metallic solids to which mechanical tests are applied may be very roughly listed as follows:

(*a*) plastics and rubbers
(*b*) fibrous materials (paper, wood, textiles, etc.)
(*c*) glasses
(*d*) building materials (concrete, stone, cement, etc.) and ceramics.

This classification is of course neither exhaustive nor free from overlap, but it is convenient in that many of the members of each group tend to have rather similar mechanical characteristics so that similar methods of test can be employed. It is proposed to mention briefly the type of mechanical properties associated with each group and discuss the particular problems which arise in carrying out mechanical tests on them.

(*a*) *Plastics and rubbers.* The outstanding difference between the mechanical behaviour of these materials and that of solids built from simpler molecular units is the very much greater sensitivity of the former to the rate at which stresses are applied to them. Thus Young's modulus for a steel wire could be determined either by hanging a small weight on the end and measuring the extension or by measuring the velocity of propagation of longitudinal elastic waves along the wire. The two results obtained would be found to agree within one or two per cent even when the stress cycle to which the material had been subjected was several hours' duration in the former experiment and a very small fraction of a second in the latter. If the same experiments were carried out with a filament of natural rubber, the two values of Young's modulus obtained would differ by a factor of perhaps a

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thousand. Similarly, the effect of temperature on mechanical properties is more marked by several orders of magnitude in high polymers than it is in non-polymeric materials. Consequently, mechanical tests carried out at one temperature and rate of loading, in general, give no indication at all of the mechanical behaviour at a different temperature or a different rate of loading. In order to map out the mechanical behaviour for a single polymer over a range of conditions, a vast amount of experimental work has to be carried out, as evidenced for example by the work of Nolle[1] on buna rubber.

In carrying out tests to cover an extensive time scale a number of widely different experimental techniques have to be employed[2] and the range covered may extend from times of the order of days or months down to times of the order of 10^{-8} s. For the longer times (>1 s) the specimen is usually loaded mechanically and either its creep behaviour under constant load, or the stress relaxation at constant extension is observed. For times of the order of one second down to about a millisecond, vibration methods can be employed. Either a specimen suitably loaded is set into free vibration or alternatively it is set into forced vibration by applying an oscillating stress. In the former case the period and the logarithmic decrement are observed whilst in the latter the mechanical behaviour of the specimen can be deduced from the value of the resonant frequency of the system and the breadth of the resonance peak.

At higher frequencies (corresponding to times between about 10^{-2} and 10^{-4} s) acoustical techniques are used, the propagation through the material of elastic waves generated by electro-acoustic transducers being observed and the mechanical properties deduced from the velocity and attenuation of such waves. The highest frequencies (up to 10^8 c/s) are investigated by studying the propagation of ultrasonic pulses through the material.

For some high polymers it has been shown by Ferry[3] that a relation exists between the effects due to change in temperature and those due to change in the period of the applied stress. Where this relation holds, the task of investigating the mechanical properties is considerably lightened in that experiments need be carried out over only a restricted time range and an extended temperature range.

The classical theory of elasticity is based on Hooke's Law, which states that the components of stress and those of strain are linearly related. Further, it is assumed that the strains are sufficiently small for powers higher than the first to be neglected. Neither of these assumptions is in general valid for high polymers. Strains large enough to invalidate the second assumption are quite usual in many polymers, whilst some of these materials, especially when they contain mineral fillers, do not appear to obey Hooke's Law even for extremely small deformations. Thus the treatment used in classical elasticity theory is in many cases no longer applicable and a new treatment is required to describe the stress-strain behaviour of such materials. This aspect of the subject has received considerable attention in recent years and an admirable account of these and other problems of rubber-like elasticity will be found in the monograph by Treloar[4] on the subject.

(*b*) *Fibrous materials.* The fibrous material which has been longest in use is timber and a large amount of empirical knowledge has been acquired about its mechanical behaviour. The mechanical properties of other members of this group such as paper, cotton, wool, silk, and the many new synthetic fibres, have been studied less extensively, but here again there is a large fund of empirical data. All these materials are composed of giant organic molecules and most of what has been said about high polymers in the previous section will apply to them. With these fibrous materials, however, there are two further factors which complicate mechanical testing.

First, these materials are often highly anisotropic, the mechanical response depending very markedly on the direction in which the stresses are applied (e.g. for balsa wood, Hearmon[5] states that the value of Young's modulus measured parallel to the grain is about sixty times as great as that measured tangential to the annual rings). Anisotropic materials require more than two constants to define their elastic behaviour and for wood which approximates to the rhombic order of crystal symmetry nine independent elastic constants are involved. As, in general, all these constants are time-dependent, a complete investigation of the mechanical properties of a single sample of timber, even if it is confined to infinitesimal deformations, is likely to prove a long and difficult one.

The second complication in assessing the mechanical behaviour of fibrous materials and especially of textiles and paper arises from the dependence of many of the properties on the mechanical interaction between fibres rather than on the inherent properties of the material of which the fibres are composed. For example, the energy lost in taking a specimen of a woven textile fabric round a stress cycle is partly due to internal friction within the individual fibres and partly to surface friction as fibres rub against each other during the deformation. Thus many of the properties may depend purely on the geometrical arrangement of the constituent fibres and it becomes extremely difficult to interpret the mechanical behaviour of the finished product in terms of the properties of the material of which it is constituted, or conversely to forecast the behaviour of a fibre assemblage from measurements of the mechanical properties of individual fibres.

A further difficulty which arises with nearly all fibrous materials is the large effect that moisture content has on their mechanical properties. The water is in general intimately contained in the structure so that the materials have to be considered as two-component systems and any theories which do not include the role of the absorbed water will bear little relation to the practical behaviour of the materials. A full account of the mechanical properties of wood and paper, much of which applies equally to other fibrous materials, will be found in the monograph by Barkas, Hearmon and Rance[5] which was referred to earlier.

(*c*) *Glass and glass-like materials.* At ordinary temperatures the elastic behaviour of glass is very simple in comparison with that of most other materials. It is unlike metals in that it does not show yield phenomena or plastic flow and it is unlike high polymers in that the strain produced is independent of the rate at which the stress is applied. It is in fact an almost perfect elastic solid which obeys Hooke's Law up to values of the stress at which it fractures. It shows evidence of elastic after-effect only after it has been highly stressed for a considerable period of time. This is also true for most other vitreous materials so long as they are at temperatures well below their softening points and the measurement of elastic properties of this class of materials affords no special difficulty. At temperatures approaching the softening point, viscous flow begins to take place and the viscosity of the material as well as its elastic modulus become important in assessing how it will behave under given stress conditions.

Most of the difficulties of investigating the mechanical properties of glass and glass-like solids are associated with the measurement of strength. As these materials are brittle and do not flow under the application of shear stresses the relevant quantity is in general the tensile strength. Now

whilst considerable variations in tensile strength are observed with most solids, measurements with glass show an exceptionally wide range of values which depend on the manner in which the specimen has been treated and how the stress is applied. First, the maximum stress which a specimen will withstand depends very markedly on the time for which the load is maintained. In the classical experiments of Grenet[6] similar specimens of plate glass were loaded for different times. It was found that when the loading time was forty hours fracture took place at less than half the stress required to produce it in a loading time of one second. Secondly, the presence of slight surface scratches can reduce the strength considerably and the value obtained for the tensile strength will depend very markedly on the surface condition of the specimen. Lastly, the size and shape of the specimen will influence the results and as shown by Griffith,[7] the value of tensile strengths of thin glass fibres may be very many times the value found with larger specimens of the same material. The subject of strength of glass has in recent years received considerable attention and reference may be made to books by Morey,[8] Haward,[9] and Stanworth[10] on this subject. Some aspects in connexion with hardness measurements are discussed later in the present paper.

(*d*) *Building materials.* This group, which includes granite, brick, slate, cement, concrete and the ceramics, covers so wide a range of mechanical properties that little of general interest can be said about methods of test. Nearly all these substances have very low tensile strengths and are normally used in compression. Young's modulus for most of these materials is of the order of 5×10^{10} dyn/cm^2, but in the case of concrete the stress-strain relation is not linear, and a tangent modulus or a secant modulus has to be employed. Accounts of the mechanical properties relevant to engineering application are normally included in works on "strength of materials" such as that by Moore.[11]

HARDNESS OF NON-METALS

In the previous section the mechanical properties discussed were quite well defined. Thus the meanings of the terms elastic modulus, tensile strength, etc., are clear for any given test and the difficulties arise only when the results obtained under one set of conditions have to be applied to a different set. In the present section the measurement of hardness will be considered, and here we have the additional difficulty of trying to interpret the significance of measurements of this property before we can see how it is likely to be affected by changing the conditions of test.

Hardness is normally defined as the resistance which a body offers to surface indentation or abrasion by other bodies with which it comes in contact, and it is difficult to relate this property in a quantitative way to the simpler mechanical constants of the material. Thus indentation hardness can be measured by the load which has to be applied to an indenter to produce an irrecoverable deformation in the material under test and such deformations may occur as a result of plastic flow, fracture or tearing. There is also a second sense in which the term hardness is used and this is as a measure of the energy absorbed when the specimen is subjected to an impulsive load. This is called the rebound hardness and, as will be shown later, it may or may not be related to the indentation hardness of the material.

The theoretical treatment of hardness depends on the classical work of Hertz[12] who first calculated the distribution of stress between two elastic bodies in contact. The Hertz theory shows that the maximum shear stress does not occur in the region of contact but at a point some distance below so that if failure results from plastic flow under a critical shear stress this will begin below the surface at a distance of the order of half the radius of the circle of contact between the indenter and the specimen. For metals this is in fact what occurs and Davies[13] has shown that the static yield point of metals may be measured by pressing hard steel balls on to the surface of the metal under test and measuring the minimum load at which a permanent deformation is produced. Alternatively the experiment may be carried out dynamically and the minimum height of fall of the ball which produces permanent deformation may be measured.

In practical tests of hardness, such as the Brinell test, a fixed load is applied to the indenter and the radius of the indentation produced is measured. For metals this, too, can be correlated with the value of the yield point under shear stress[14] and thus bears a quantitative relation to a well-defined physical property. The rebound hardness of metals is related to the work done in producing plastic flow in the metal and therefore also depends on the value of the yield stress of the material.

Most non-metals do not have well-defined yield points and many do not flow under the influence of an applied stress but fracture in a brittle manner when an indenter is pressed into them. Further, most high polymers show recoverable flow instead of, or in addition to, irrecoverable flow, and the interpretation of hardness measurements with non-metals is consequently very much more complex.

For indentation experiments with transparent high polymers the author[15] has used a photoelastic technique to show that both recoverable and irrecoverable flow take place. Whilst the recoverable flow is highly dependent on the time of loading, the irrecoverable flow, which occurs only at large loads, is associated with the non-linearity of the stress-strain relation at high stresses. Indentation experiments with glass specimens showed no evidence of flow and here fracture occurred in the region round the indenter where the tensile stress is a maximum. Since the stress field can be evaluated by Hertz's theory it might be thought that the minimum indenter load which produced fracture could be simply related to the tensile strength of the material. This was first attempted by Auerbach[16] who found that the tensile strength calculated in this way was inversely proportional to $r^{\frac{1}{3}}$ where r is the radius of curvature of the indenter. This anomaly has been explained as being a statistical effect due to the flaw distribution in the specimen. The argument runs that with indenters of smaller radius of curvature the area of contact is smaller and hence the probability of finding a surface flaw in the right position to start a crack is reduced. Recent work[17, 18] by two of the author's colleagues has shown that this explanation is incorrect and that whether or not a fracture is formed is normally governed by the availability of stored elastic energy in the specimen. Griffith[7] first pointed out that for a fracture surface to grow, some of the stored elastic energy must be able to be converted into the surface energy of the new fracture area, and in indentation experiments this is generally the relevant criterion. Only when indenters of large radius of curvature are employed (>10 cm for steel indenters on glass) does fracture depend solely on a critical tensile stress being built up round the region of contact. Thus in indentation experiments on glass-like materials two distinct mechanical properties are involved. One is the tensile strength in the macroscopic sense, the other is the energy associated with forming a new fracture surface; in some tests it is one and in some the other that is being measured.

Measurements of rebound hardness are in practice carried out with an instrument called a scleroscope in which the height of rebound of an indenter is measured after the indenter has fallen a known distance. The principle of the method is that part of the kinetic energy of the indenter will be lost in plastic deformation of the specimen and hence the height of rebound will be a measure of the resistance of the specimen to indentation. Plastic flow is, however, not the only way in which the energy of the indenter may be dissipated. When the indenter hits the specimen stress waves are set up in the latter. Whilst for specimens of large dimensions the energy lost in this way is only one or two per cent of the kinetic energy of the indenter, the losses due to this effect may become considerable for specimens whose thickness is comparable with the dimensions of the indenter. Zener[19] has investigated this phenomenon theoretically and Tillett[20] has confirmed the effects experimentally. Only for specimens which are sufficiently large for the stress waves reflected from their boundaries not to have had time to return to the region of contact before the indenter and specimen separate, is the rebound height independent of the dimensions of the specimen. When the specimen is thinner, so that the stress wave is able to traverse the thickness of the specimen several times during the period of contact, the energy loss due to the flexural motion set up may be many times the losses due to inelastic behaviour in the material; the rebound height then becomes a measure of the thickness of the specimen rather than of the physical properties of the material.

When precautions are taken to ensure that losses due to elastic waves in the specimen and to adhesion between the indenter and the specimen are small, the results of rebound measurements on metal specimens can, as shown by Tabor,[14] be correlated with the yield strength and hence with the indentation hardness of the metal. For non-metals, in which plastic flow does not occur, the coefficient of restitution measured in rebound measurements must clearly depend on different physical properties. At the instant during the impact when the indenter is at rest its kinetic energy has been entirely stored in the form of elastic strain energy, partly in the indenter and partly in the specimen. In most practical cases the energy stored in the indenter is very small and the specimen is thus taken through a stress cycle the duration of which is equal to the duration of the impact and the coefficient of restitution is a measure of the fraction of energy lost in the cycle. This can be related[2] to the internal friction measured in other ways. Jenckel and Klein[21] and Tillett[20] have shown that for high polymers and organic glasses the observed coefficient of restitution is in fact a measure of the internal friction of these materials for sinusoidal stresses at frequencies equal to the reciprocal of approximately twice the time of contact.

CONCLUSION

It is hoped that the few examples discussed have illustrated the complex nature of the mechanical testing of non-metals and have shown that a proper interpretation depends on a fuller understanding both of the mechanical properties of these materials and of the theory of the tests. This is a field of enormous practical importance and one in which the physicist has a place at least as prominent as that of the engineer. The latter has perhaps rested too long in the comfortable belief that the accumulated body of experience on strength of materials will cover any testing problems he may encounter, whilst the former has too often assumed that all the important problems connected with properties of matter were solved at some time during the last century. With the advent of so many new materials and new conditions of loading, neither of these views is likely to prove tenable.

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Symposium on optical and surface methods of non-destructive testing

In Paper 1 of this symposium Prof. Tolansky reviews the optical methods used in his laboratory for the examination of micro-structures of metal surfaces. The methods described are two-beam interferometry, multiple-beam interferometry, the light-profile microscope, optical shadow casting and the total reflexion contact method. The usefulness and limitation of each method is discussed. Examples of the application of each method are given.

In Paper 2 by Dr. Stephens the various types of optical measurement which might be applied to the examination of surfaces are briefly discussed. Consideration is given to the possible use for specific problems of the ultra-violet, the visible, the infra-red and the microwave regions of the electromagnetic spectrum.

Paper 3 is a brief survey by Dr. Heavens of the type of information which may be obtained by the application of optical methods to the study of the surfaces of materials. Consideration is restricted to the kind of method which is likely to be of use as a non-destructive test.

Paper 1. By PROF. S. TOLANSKY, D.Sc., F.Inst.P., F.R.S., Department of Physics, Royal Holloway College, University of London.

The non-destructive testing of metals by optical methods is a very wide field. In this survey I will restrict myself to a brief description of some of the experimental work in this subject carried out in my laboratory during the past few years. It is usual to interpret the term "non-destructive" rather widely. Thus the production of some local micro-damage, such, for instance, that which occurs during micro-hardness testing is generally accepted as a non-destructive test, although there is clearly some slight destructive damage.

I have used successively five different methods of approach and these can be described as follows: (*a*) two-beam interferometry, (*b*) multiple-beam interferometry, (*c*) the light-profile microscope, (*d*) optical shadow casting, and (*e*) total reflexion. Here the discussion will mainly be devoted to a consideration of the possibilities and limitations of these different methods.

TWO-BEAM INTERFEROMETRY

Two-beam interferometry has been widely used for the evaluation of surface topography since its first application to this by Laurent in 1886, in connexion with glass surfaces, although for some time Fizeau fringe systems have been used for figuring and standardizing metal gauge blocks. The visibility of such fringes (metal matched against glass) is usually poor.

Interference fringes have the property of high resolution and high magnification in the height-depth direction only, and with a metal-glass system, topographical features smaller than 1/10 of a fringe separation (say 250 Å) can hardly be evaluated. However, two-beam interference systems have the important characteristic that one can use high lateral magnification (say up to $\times 1500$) from say a 3 mm objective of N.A. 0·95 with no effective loss in definition. A notable example of an instrument employing 4 mm lenses is the Linnik interference microscope. This is essentially a Michelson interferometer, arranged with two high power microscope objectives, one imaging a flat, the other imaging the metal object and with it excellent fringe visibility can be secured.

Such a system can be considered at its best to resolve a flat parallelopiped which is in extension a square of side $\lambda/2$ and of depth $\lambda/20$. There are many metallurgical problems wherein knowledge about so small a volume element is very useful indeed.

MULTIPLE-BEAM INTERFEROMETRY

In the up-down direction an entirely higher order of magnitude of sensitivity obtains by the use of multiple-beam interference methods. Quite a number of different multiple-beam techniques are now available for specific applications. They all have this in common, namely that the shape of interference fringes can be profoundly modified by the deposition of highly reflecting coatings on the two surfaces to be used for the production of interference. With correct attention to optical conditions it is easily possible to secure fringes whose width is less than 1/50 part of the separation between orders, i.e. the fringe width is a mere 50 Å. Displacements of about 1/5 of a fringe width can just be resolved, i.e. 10 Å. Indeed in special instances a still smaller quantity can be resolved. It is remarkable that with such very simple (but precisely controlled) means it is possible to resolve quantities in the up-down direction of the order of crystal lattice spacings. This is, of course, a consequence of the advantageous intensity distribution in the fringe system produced by a correct multiple-beam optic.

It has also been established in my laboratory that the examination of opaque bodies (including, of course, metals) is facilitated by the employ of multilayer reflectors as an alternative to silver. For it can be shown that the visibility (i.e. contrast) in reflexion fringe patterns is determined primarily by the absorption coefficient of the reflecting film (the narrowness, i.e. width, is the parameter which is affected by the reflectivity). Now dielectric multilayer high reflectors (zinc sulphide and cryolite $\lambda/4$ layers) have very low absorption and are therefore well suited indeed for use for the examination of metals by reflexion fringes.

With regard to the magnification in extension which can be used, this depends critically upon the nature of the surfaces under study. The prime controlling condition is the necessity for having the two interfering surfaces very close to each other. Indeed, for the highest powers the separation must not exceed one wavelength of light. Of course, the character of the topography determines the ultimate closeness of approach for if there exist projections (hills) then the valley regions are of necessity some distance below the optical flat. (In obstinate cases a replica can be taken which reverses hills and dales and thus valley regions become amenable also to precision attack.)

When conditions permit it has been found possible to employ the high power of a 3 mm dry objective, N.A. 0·95, used at $\times 1500$ and still obtain very sharp fringes. Indeed, in the best picture yet secured in my laboratory lateral resolution was such that 0·75 μ could be resolved and 50 Å

could be resolved in depth. This means that a volume element of some 3×10^{-15} cm^3 has been evaluated. Clearly so powerful a technique has obvious application in many branches of metal physics and small regions, e.g. corrosion pits, can be detected and measured.

One strikingly important application of multiple-beam interferometry is the way in which it can be used, not only for the measurement of microtopography, but equally as a contrast-enhancer, revealing subtle surface detail which can escape even phase-contrast microscopy.

A brief enumeration of some non-destructive testing data on metals secured in my laboratory with multiple-beam interferometry will suffice to show what can be achieved.

Data on crystal topography obtained include:

(1) Cleavages of single crystals (e.g. zinc, bismuth). The fringes reveal the cleavage mechanism.
(2) The shapes and distributions of etch pits on alloys.
(3) The mechanism of cathode etching and the actual structure and topography of the grain boundaries in several alloys (e.g. tin–antimony alloys).
(4) The shapes of the changes in grain boundary on thermal etching.
(5) Surface topographies of dendritic growth crystals (e.g. germanium dendrites and tin dendrites deposited from solution).

A good deal of work has been carried out too on the surface changes accompanying indentation and machining of metals. This includes:

(1) Examination of the flow of metal surrounding hardness indents. Diamond indenters (ball, cone, pyramid) have been used with a wide range of typical alloys, and flow patterns evaluated.
(2) Directional hardness, directional flow and distribution of slip has been studied for indented single crystals of tin and of bismuth.
(3) Polished and electropolished surfaces have been examined for topographical structure.

Another field of some promise in which some work has already been done concerns electro-plate. Thus the contouring efficiency of a brightly deposited electro-plate (Sn–Ni) has been interferometrically studied. Again, hardness indentation experiments have been made on hard alloy electrodeposit coatings (e.g. speculum and tin–nickel) and the break-up of a fractured film studied interferometrically. It is unnecessary to multiply examples, for it will be recognized that this technique has much to offer.

A field of particular value is that of the evaluation of the thicknesses of thin films of metals. Interferometry has added appreciably to our knowledge of thin films by offering an accurate method for measuring film thicknesses down to about 25 Å.

LIGHT-PROFILE MICROSCOPE

I come now to the light-profile microscope, developed in 1952. This is related to, but a considerable improvement on, the Schmaltz double microscope light-cut technique. This is a technique admirably suited to many metallurgical problems. It is particularly easy to apply if one has available a Vickers metallurgical type inverted projection microscope. The method is simple. The surface under examination is viewed with a 2 mm oil immersion objective, although, of course, lower powers can be used. The illumination must not be incident normally but off-centre (the built-in off-centre metal sector tongue reflector in the Vickers instrument exactly meets requirements). In front of the microscope field lens lying between objective and light source is placed a piece of glass with a narrow scratch (or several parallel scratches) on it. The result of this is that a sharp shadow can be cast (at some 45° incidence) on to the surface. This shadow profiles the surface contour, displacing say to the left when crossing a rut and to the right when crossing a ridge. Thus surface topography is revealed. It can be arranged so that in a surface viewed say at $\times 1000$ the profile magnification sideways and in depth is the same. If then the profile, in passing over such a rut, displaces 1 mm, then the depth of that rut is 1 μ. With a correct optic it is possible to resolve easily 0·25 μ in all three dimensions, a very useful feature indeed in connection with many metallurgical problems, especially those associated with machining processes. The method is essentially simple and non-destructive. As an indication of possibilities the following lists some of the studies already made in my laboratory with light-profile microscopy.

(1) The topographical profile was secured for soft alloy shell bearings (automobile engines). These were too soft to tolerate a diamond stylus test.
(2) Depths of hardness indentations have been studied and recovery effects detected and measured.
(3) Etch and corrosion pits have been evaluated, both the shapes and depths being revealed.
(4) The thicknesses of electrodeposits have been measured with the profile.
(5) The rate of removal of material both by chemical etch and glow discharge cathodic etch has been evaluated.
(6) Useful data have been secured on machine finishing processes such as cutting, milling and grinding.
(7) The profiles of line gratings have been secured, a matter of much value in connexion with the "blazing" operation.

Further applications are obvious. The magnifications available are under control and vary conveniently from $\times 200$ to $\times 2000$. It will, of course, be appreciated that the light-profile is of a lower order of sensitivity than multiple-beam interferometry, but that is its special advantage. For many technological surfaces are just too rough for precision interferometry and this is precisely where the profile system steps in.

OPTICAL SHADOW CASTING

I shall now, very briefly indeed, consider what I call "optical shadow casting." This is a technique devised for still coarser surfaces, of the type often met with in growing crystals (which can at times be relatively quite rough).

A particle on a plane surface, if illuminated at a grazing angle of say 3°, throws a shadow of length which is some 20 times the height of the particle. If viewed with a microscope at say $\times 200$, the shadow length (if visible) is then 4000 times the height and thus small heights can be measured. Of course, diffraction restricts the smallness of the height that can be studied and in any case leads to a fuzzy edge of the shadow, introducing a certain amount of error in estimating the length (usually some 5% or so).

Now in fact a shadow will only be seen if the particles are on a fine-grain scattering surface which scatters light up (almost through 90°) into the microscope. Since in any event such scattering will be weak, a very intense source is needed.

I have found an ideal scattering source is a very thin

Fig 1

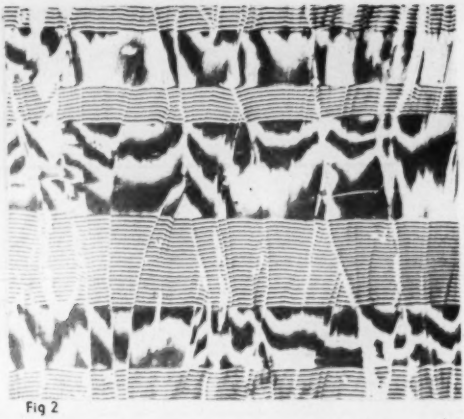
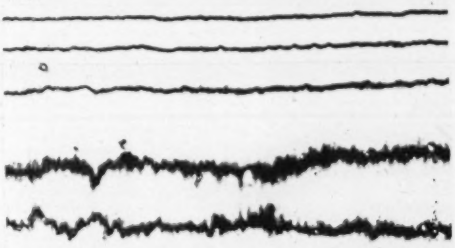


Fig 2



a

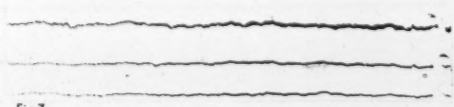


Fig 3

Fig. 1. Two-beam fringes with a glass plate (×20)

Fig. 2. Unsilvered fringes, twin bands on bismuth (×100)

Fig. 3. Multiple-beam fringes showing micro-structure of super-finished ground metal cylinder (×250)

Fig. 4. Multiple-beam fringes, cleavage of zinc crystal (×75)

Fig. 5. Surface of a titanium crystal (×720)

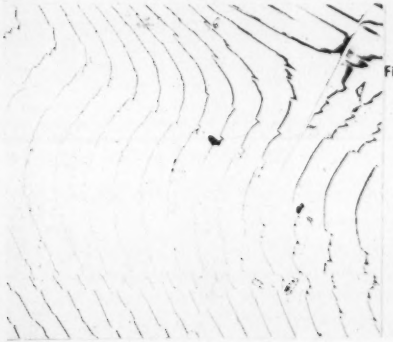


Fig 4

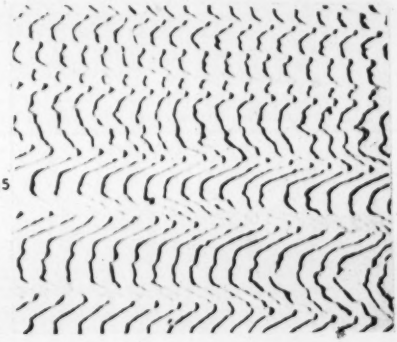


Fig 5

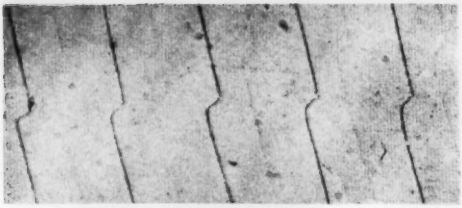


Fig. 6. Multiple-beam fringes measuring thickness of a metal film 520 Å thick (×10)

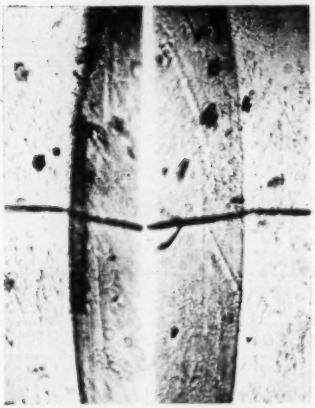


Fig. 7. Light-profile on an indent on a metal surface (×700)

Fig. 8. Multiple light-profile on machined Babbitt bearing surface (×1500)

Fig. 9. Light-slit pattern showing "blazing" on an infra-red grating (×1000)

Fig. 10. Shadow-casting pattern on a zinc cleavage using coarse magnesium oxide coating (×100)

deposit of silver which has been exposed to the vapour of *aqua regia*. Alternatively a thin smoke cloud from a burning magnesium ribbon can produce an adequate surface, and with such surfaces, sharp well-defined shadows can be formed.

For examination of a crystal or metal the scattering surface is created *in situ* on the metal itself and on correctly illuminating, the shadow patterns appear. With these it is possible to measure growth ledges, growth pits, etch pits, etc. Furthermore the intensity oblique illumination enhances contrast of ledges and edges in a very striking way.

The lower limit appears to be of the order of 2 μ, for diffraction troubles become difficult at this stage. Thus the method is relatively coarse. As yet it has not been fully exploited and remains as a method with interesting future possibilities.

TOTAL REFLEXION

Finally, in completing this survey a very brief review will be given of the total reflexion method which has been advocated in France and Germany (e.g. by Mechau).

When using a totally reflecting right-angled prism, light enters one face, reflects from the hypotenuse face and then emerges from the third face. Now if the reflecting hypotenuse is pressed on to a metal surface, where there is intimate contact between prism material and metal, the total reflexion is interfered with. This is because a totally reflecting wave partially penetrates the boundary. Suppose the metal surface is machined, say with a lathe. It has a number of high spots. These contact the glass and appear as dark regions in the total reflexion picture. In effect then the prism reveals what the engineer calls the "bearing surface." Such a bearing surface is that which is involved in the friction of sliding parts and is of importance in technology.

I have examined this technique using a specially ground right-angled prism made from diamond. This has been chosen since clearly one can expect distortions at small points of contact where the applied (even small) loads can lead to quite high stresses. If one has a diamond prism this is so hard that one variable at least is eliminated, for the prism itself does not then distort.

Of course distortion of metallic asperities is bound to occur and this is clearly a serious defect of the method. Indeed, I am as yet not quite happy about the results of the technique. I set up a microscope which gave a light-profile picture of a machined surface and then obtained a total reflexion bearing surface picture of the same region. Correlation was somewhat poor.

It is likely that several factors tend to falsify the total reflexion method. Apart from the obvious flattening of asperities (an undesirable feature, of course) there seem to be complex phase reflexion effects which require further study. Thus I find that the use of polarized light changes the observed pattern. Again the deposition of thin metal films on the hypotenuse seems to affect the results.

In short, although the method has been strongly advocated by one or two continental protagonists, it requires a good deal of careful optical examination first, before being widely adopted.

A serious drawback in any case is the purely qualitative nature of the picture revealed. Only regions of contact (and their artificially flattened out extensions) can be seen. Nothing is known about the depths of valleys in between and certainly nothing is known about the heights of asperities before they were flattened by the prism. The method is much inferior to the light-profile microscope.

In conclusion a number of illustrations are appended showing some examples of the applications just considered above.

Paper 2. By R. W. B. STEPHENS, Ph.D., D.I.C., F.Inst.P., Imperial College of Science and Technology, University of London.

Plane polarized light incident on a reflecting surface experiences a small angular rotation of its plane of polarization. The improvement in measurement techniques of optical rotation has focused attention on the possibility of utilizing this effect for the non-destructive testing of metallic and other opaque surfaces. The rotation gives a measure of the energy loss in a dissipative material. In certain alloy systems, e.g. silver-gold, copper-nickel, the change of reflectivity with composition is particularly favourable for using the total intensity of the reflected light as a means of testing the departure of such substances from a standard composition. The employment of photomultiplier cells as light detectors permits optical reflexion tests to be automatically controlled.

In the case of high polymers the optical index of refraction increases as the degree of polymerization increases, and double refraction effects can be used to indicate anisotropy in such materials. Another optical method, which perhaps is only partially non-destructive in operation, is that involving the spectroscopic examination of an electric spark (or arc) passed between the metal test surface and a counter electrode.

It must be emphasized that the general usefulness of optical reflexion methods is dependent upon good reflecting surfaces. Since the depth of penetration of the light wave is only of the order of a few hundred Ångström units, any surface treatment made to obtain better smoothness is liable to alter the measured surface properties, which will then differ from those of the bulk material. If the nature of the test is to compare the smoothness of a surface with that of a standard then our "probing" wavelength should be in the violet, i.e. the shorter wavelength end of the visible spectrum. On the other hand if our concern is with the composition of the test material then, other considerations being equal, it would be desirable to employ longer wavelengths which would thus tend to eliminate the effect of the smaller surface blemishes. In this connection the use of obliquely incident light ("cos θ" effect) will minimize the effect of surface undulations. The use of longer wavelengths suggests infra-red radiation, and here with suitable sources advantage may be taken of the recent developments in photo-conductive cells, e.g. lead sulphide, lead telluride, etc., with their small time-constants.

A class of experiment which seems to have been little explored is the use of other physical agencies, made complementary to the observed optical phenomena. Typical of these are the Kerr magnetic and electrostatic effects. In the former plane-polarized light reflected from a metallic surface becomes elliptically polarized on the application of a magnetic field. The ready availability of strong permanent magnets and high voltage apparatus may make such methods a worthwhile investigation.

Proceeding to still longer wavelengths in the electromagnetic spectrum we come to the microwave region and the possibility of utilizing reflectivity measurements with electromagnetic waves. An accuracy of approximately 2% has been claimed for reflectivity measurements with 1 cm waves. By employing electromagnetic radiation over a range of wavelengths, and thus varying the depth of penetration within the

conducting surface, useful information regarding the homogeneity within the surface layers might be provided. Interest has recently been revived in the laboratory generation of electromagnetic surface waves, i.e. electromagnetic radiation incident on a surface at the Brewster angle gives rise to a wave system which will cling to the surface. These Sommerfeld or Zeeneck waves are attenuated both in the direction of propagation and also normal to the surface. Since this attenuation is a function of the reactance of the surface it will be dependent on geometrical irregularities and on surface composition. These surface waves are propagated if a thin dielectric layer covers the underlying metal but the presence of a break in this layer will lead to the "blocking" of the surface waves, and it is suggested that this effect might find some specific application in surface flaw detection.

Paper 3. By O. S. HEAVENS, B.Sc., Ph.D., F.Inst.P., Royal Holloway College, University of London.

INTRODUCTION

The purpose of this paper is to summarize the types of information which may be obtained by the application of certain optical techniques to problems of non-destructive testing. Since optical methods leave the material (with the exception of such things as photographic emulsions) unchanged, they are non-destructive in the strictest sense of the word. In cases in which they can be applied without special preparation of the specimen under test they may therefore possess some advantages over existing methods. Attention will be confined to procedures which are not, as far as is known, used as standard methods of test since these methods are adequately described in various standard works on optical testing methods.

It is convenient to consider separately the cases of transparent and of opaque materials. In respect of transparent materials, there exists already a large number of established testing methods, which have been developed to an impressive standard of sensitivity by the optical industry. Standard interferometric techniques, embodied in such devices as the Fizeau interferoscope and the Twyman–Green interferometer, enable such properties as surface finish, optical homogeneity and geometrical conformation of products to be tested to within very fine limits. Certain of these methods can be applied by employing replica techniques to the examination of opaque materials. An example of this development is illustrated by the work of Dyson, in which interference microscopy has been applied to the problem of surface finish on gears.[1] In view of the nature of the problem of non-destructive testing, it would seem wise to concentrate on methods which can be reasonably easily applied and which lend themselves to automation. Methods in which the assessment and interpretation of results is lengthy and difficult are unlikely to prove very useful.

OPTICAL REFLECTIVITY

Transparent materials. Simple electromagnetic theory enables the behaviour of beams of radiation which are reflected by, or transmitted through, materials to be calculated exactly. The theory is simple, however, only for situations which are never met practically. The case of a perfectly homogeneous isotropic material with a mathematically plane surface leads to quite simple expressions for reflectance and transmittance. Even with anisotropic materials, the treatment remains fairly simple. Since, under close inspection, real materials do not conform to these idealizations, we shall not expect predictions to be followed rigorously by the experimental observations. We are, in fact, able in certain cases to obtain information about the structure of the material by observing the departures from simple theory which are shown by the experimental results.

Let us summarize the results of applying electromagnetic theory to the case of the reflexion of light at the plane surface of a homogeneous, isotropic, non-absorbing medium. The reflectance of a surface at non-normal incidence depends on the state of polarization of the incident light. For light polarized with the electric vector parallel to the piane of incidence (*p*-component) the reflectance (ratio of reflected to incident *energy*) is denoted by R_p. For reflexion in vacuum at the surface of a material of refractive index n, at an angle of incidence θ_1,

$$R_p = \left(\frac{\cos\theta_2 - n\cos\theta_1}{\cos\theta_2 + n\cos\theta_1}\right)^2 = \frac{\tan^2(\theta_2 - \theta_1)}{\tan^2(\theta_2 + \theta_1)} \qquad (1)$$

where θ_2 is the angle of refraction. $\sin\theta_2 = \frac{1}{n}\sin\theta_1$. For light polarized with the electric vector perpendicular to the plane of incidence (the *s*-component),

$$R_s = \left(\frac{\cos\theta_1 - n\cos\theta_2}{\cos\theta_1 + n\cos\theta_2}\right)^2 = \frac{\sin^2(\theta_2 - \theta_1)}{\sin^2(\theta_2 + \theta_1)} \qquad (2)$$

Curves of R_p and R_s against θ_1 are shown in Fig. 1.

For $\theta_1 = \arctan n$, $R_p = 0$. This angle of incidence is known as the Brewster angle θ_B, and is easily measured by

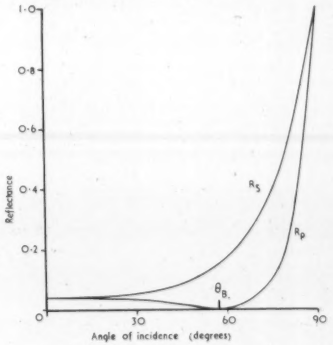


Fig. 1. Variation of R_p and R_s with angle of incidence for a transparent medium of refractive index 1·5

reflecting plane polarized light (the *p*-component) from a surface and adjusting the angle of incidence for a minimum of reflectance. This type of measurement lends itself readily to automatic methods: the angle of incidence could, for example, be scanned over a small range and the angle for minimum reflectance indicated. Simple apparatus should enable any gross variation—e.g. from batch to batch of material—to be detected.

The reflected beam generally differs in phase from the incident beam. For the *s*-component the change in phase on reflexion remains constant at π for all angles of incidence.

That of the *p*-component changes abruptly by π at (for the idealized case under consideration) the Brewster angle. The difference between the phase changes of the *p*- and *s*-components (differential phase change Δ) may be measured to within a few minutes of arc. In practice, the variation of Δ with angle of incidence is observed to be continuous, as illustrated by the curve in Fig. 2. The polarizing angle θ_p is defined as the angle at which the differential phase change is $\pi/2$. For the ideal case, θ_p and θ_B should coincide: in general they are found to differ quite measurably.

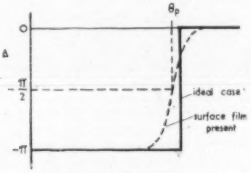


Fig. 2. Variation of Δ with angle of incidence

The presence of surface films or of mechanical strain in the surface gives rise to the observed departure from simple theory and the observed differences may be useful in detecting such surface inhomogeneity.[2] Very sensitive methods of examining the state of polarization of light beams are available: this is largely because relative rather than absolute measurements are involved. One common method is to illuminate the surface with a parallel beam of light with the plane of polarization inclined at 45° to the plane of incidence. A Nicol or other prism serves as polarizer. The reflected light (which for the ideal case should be plane polarized) is elliptically polarized and this ellipticity is measured. This is effected by introducing into the reflected beam a birefringent compensator, such as the Soleil–Babinet or the Senarmont, and adjusting the phase difference introduced until the reflected beam can be extinguished by means of an analyser. The ellipticity of the reflected light is then easily found from the angle between the restored plane of polarization and the plane of incidence (Ditchburn).[3] Ellipticities corresponding to the presence of surface films or inhomogeneities a few Ångströms in thickness are detectable.

If homogeneity on a coarser scale is present, then use may be made of a simple relation which exists between the *p*- and *s*-components in the reflected beam. For an angle of incidence of 45°, $R_p = R_s^2$, a result readily obtained from equations (1) and (2). Absolute measurement of reflectivity is required so that the sensitivity of this criterion of homogeneity is lower than that obtainable by ellipticity measurements. It should be emphasized that this is a criterion of optical homogeneity and not of surface smoothness. The relation $R_p = R_s^2$ will not hold for a surface in which there is a gradient of optical properties normal to the surface even though the latter may be plane. This criterion has been applied by Schulz[4] in studies of films formed by thermal evaporation. For films of silver and aluminium this relation is found to be obeyed only after suitable heat-treatment: for films of lead and tin (which are known from electron microscope evidence to be much less homogeneous than silver or aluminium) values of R_s^2/R_p as low as approximately 0·3 were observed, even after heat-treatment.

Mention may be made here of a simple result concerning the reflectance of a surface partly covered by a transparent film of index n_f. For light polarized with the electric vector in the plane of incidence the reflectance at an angle $\theta = \arctan n_f$ is the same on the filmed and unfilmed parts of the surface. This affords a simple method[5] of determining the refractive index of surface films—under favourable conditions with an accuracy of $\pm 0{\cdot}002$. A suitable experimental arrangement is shown in Fig. 3. The condition of equal reflectance is independent of substrate index and of film thickness: the sensitivity of the method does, however, vary with the film thickness. It is desirable that the refractive index of the substrate be not too different ($\gtrsim \pm 0{\cdot}3$) from that of the film.

Absorbing materials. The reflectance at the surface of an absorbing medium may be determined in terms of the real and imaginary parts of the complex index $\boldsymbol{n} \equiv n - ik$. k is known as the extinction coefficient. Considerable care is necessary in dealing with quoted values of this quantity since $\boldsymbol{n}$ is sometimes written $n(1 - ik)$. In the general case,

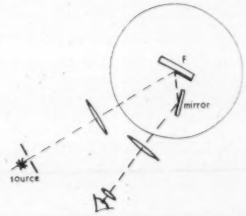


Fig. 3. Arrangement for measuring the refractive index of a film. The telescope is focused on the film *F*

the determination of n and k from reflectance measurements is not possible explicitly. However, for many metals, for some part at least of the visible spectrum, $n^2 + k^2 \gg 1$ in which case n and k can be determined fairly easily. The differential phase change is neither zero nor π so that incident plane polarized light is reflected in an elliptically polarized state. The angle of principal incidence Θ is defined as that for which $\Delta = \pi/2$. At this angle of incidence, insertion of a quarter-wave compensating plate, suitably orientated, converts the elliptically polarized light to plane polarized—a condition readily and sensitively detected. The angle Φ (principal azimuth) between the vibration direction of the restored plane polarized light and the plane of incidence is also determined. The optical constants n, k are then given by:[3]

$$n = \sin\Theta \tan\Theta \cos 2\Phi$$
$$k = \tan 2\Phi / n$$

For the condition under which the above approximations are valid, the depth of penetration of the light wave is very small ($< \lambda$) so that the values obtained are characteristic of the surface layers only. This measurement needs, moreover, a good quality optical surface which can be produced generally only by disordering the surface layers by polishing. If this is removed by etching, the resultant surface is generally not of sufficiently good optical quality to enable this type of measurement to be made. In order to be of use as an indication of the state of the (bulk) metal, it would be necessary to obtain by some independent means a correlation between the structure and the surface constants. One possibility might be to move into the near infra-red region where, on account of the longer wavelength, the surface irregularities produced

by etching may be unimportant. (Although it is generally assumed that the optical constants of surface layers differ from those of the bulk, the comments of Roberts[6] indicate that this may be an open question.)

For the spectral regions where n is small and k large, the value of k depends predominantly on the number of free electrons whereas n depends mainly on the surface conductivity (Schulz).[4] n is therefore more sensitive to surface disorder or strains. This feature is illustrated by the results obtained for n and k on metals, in which it is found that the values of n depend more markedly on the surface preparation than do the k values. This argument holds, however, only if the crystallite size is not very small compared with the wavelength. In very thin (< 100 Å) evaporated films of metals containing small, separated crystallites, the optical constants show a reversal of the normal metallic behaviour. The value of n becomes large and the k-value small.

SURFACE ROUGHNESS

The methods used to determine the smoothness of a surface depend very much on the scale of the irregularities present. It is convenient to consider, somewhat arbitrarily, three regions made up as follows: (1) the irregularities are on such a scale as to cause measurable scattering of an incident light beam, (2) the irregularities are of the order of visible light wavelengths, and (3) departures from smoothness amount to a small fraction of a wavelength.

For region (1), the amount of scattering may be used simply as an empirical measure of the surface roughness. A useful quantity in this connection is the ratio of the specular to the total reflectivity since this quantity depends, to a first approximation, only on the smoothness of the surface and not on the absolute value of the reflectance or on the wavelength of the light used. The integrating sphere optical smoothness meter described by Guild[7] may be used for such measurements. Provided the usual precautions are taken (e.g. of stabilizing the light source) a high sensitivity is achieved and roughness which is too small to be detected visually may be measured.

For region (2) where irregularities are too small to scatter visible light, two-beam interference methods may generally be employed. In the working of optical surfaces, the geometrical shape may be accurately determined by the observation of interference fringes between the test piece and a reference surface. The smoothness of the fringes gives an indication of the state of the surface to the order of tenths of a fringe. Direct methods of this type, such as are used, e.g. for testing slip gauges, have a low lateral resolution. The high resolution normal to the surface is combined with microscope resolution laterally in the several forms of interference microscope now available, by means of which irregularities in optical path considerably less than $\lambda/100$ can be detected.

In region (3), for the examination of surface smoothness on the finest scale, there are two methods giving very high resolution normal to the surface. Multiple-beam interference methods may be used at high lateral magnification. Thus in the examination of diamond surfaces multiple-beam Fizeau fringes have been used at a lateral magnification of $\times 1500$ (Tolansky and Emara).[8] These methods require that the surface of the specimen possess a high reflectance. A reference flat, covered either with a silver film or a high-reflecting multilayer, is brought as close as possible to the specimen surface and the surface viewed by collimated monochromatic light. (Alternatively, white light is used and the surface imaged on the slit of a dispersing system.) The method is of general application, for transparent surfaces (suitably coated) or for opaque materials, requiring only that the surface be reasonably flat microscopically over the area of the reference flat.

A second method giving high sensitivity is that employing phase contrast techniques. These methods have been used for many years for the testing of lenses and mirrors and have the advantage over the earlier Foucault test that they show irregularities of profile directly in terms of intensity variations in the image of the surface examined. A typical arrangement of the apparatus is shown in Fig. 4. The test

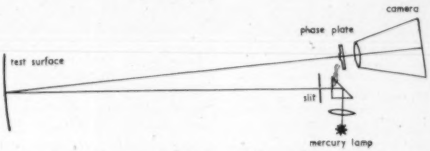


Fig. 4. Lyot's arrangement[9] for examining surface finishes by phase contrast. The slit width is 0·1–0·2 mm. The camera is focused on the test surface

is highly sensitive, enabling departures from the correct figure of the surfaces of a few Ångström units to be detected easily. It is of use, however, only if the departures which are present are very small.

Of general application is the phase contrast microscope. This has been applied over a very wide field and has enabled information to be obtained under many conditions where amplitude-contrast methods are of no avail. In favourable circumstances a region in a specimen which differs in refractive index from that of the surroundings by only one or two units in the fourth decimal place may be observed by phase-contrast techniques. For the examination of metal surfaces, two methods are available. For surfaces showing high specular reflection a vertical phase illuminator provides the most sensitive viewing arrangement. For metal surfaces which give rise to appreciable scattered light, transparent replicas may be used with the conventional phase contrast microscope. A wide range of phase-plates is now available commercially. In many cases it is necessary to determine by trial and error the most suitable phase-plate for any particular problem. An excellent indication of the range of problems for which this method is suitable is given by Bennett.[10]

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The potentialities of X-ray diffraction studies in non-destructive testing

By J. R. Raiт, D.Sc., F.I.M., and H. S. Peiser, M.A., F.Inst.P., Hadfields Ltd., Sheffield

The concept of a non-destructive test is defined. One of the criteria—that the purpose of examination be to relate past history of a particular specimen (or group of specimens) with expected future service performance—is not fulfilled by much conventional X-ray diffraction work. Nevertheless, five groups of X-ray diffraction tests are useful in non-destructive examinations: (i) X-ray fluorescent spectrometry in chemical element analysis; (ii) X-ray diffractometric phase analysis; (iii) X-ray measurements of orientation textures; (iv) precision X-ray determinations of lattice parameters which depend on solid-solution, temperature and strain effects; (v) X-ray determinations of line profiles related to crystal size and perfection.

Conventional X-ray diffraction tests suffer from (*a*) insensitivity to localized, but physically significant lattice defects, and (*b*) restrictions due to the smallness of surface volumes examined. The latter short-coming is overcome by high-voltage diffraction testing which, however, is limited to coarsely-grained materials. For these it provides a non-destructive grain-size test.

Polychromatic streaks (asterism) on high-voltage diffraction pictures are interpreted in terms of small changes of lattice orientation within grains due to strains or polyganization. Absence of streaks implies a high degree of grain perfection which is lost under diverse types of service conditions such as those causing fatigue in metals.

Introductory remarks on the concept of non-destructive testing

Having been privileged to hear and read some of the deliberations of the Non-Destructive Testing Group's Physics Sub-Committee we felt that, at a time when the Group was taking stock of the fundamental physics inherent in actual and possible non-destructive testing methods, a general paper on X-ray diffraction applications was opportune and could be coupled with our experimental results in high voltage diffraction effects.

The concept of a non-destructive test is not entirely straightforward, and is the subject of an introductory discussion: voltage measurement in an electric circuit, to give a simple example, is non-destructive of the existing electrical flow and the material making up the circuit. This is typical of almost all experimental natural philosophy that aims at making observations of natural phenomena without appreciably upsetting the phenomena themselves through the act of observation. In this fundamental sense most scientific measurements aim at being non-destructive. Obviously the Group is concerned with a more restricted field of science. The Chairman explains that it is only concerned in the physical non-destructive testing of materials. This is an important restriction.

We must not, however, be too literal in our interpretation of "non-destructive," and to give another, not very serious example, the incidental fact that a doctor measuring the sedimentation rate on a representative sample of blood does not find it practicable, safe or worth-while to re-inject the used sample into the blood stream of the patient, should not in itself exclude the measurement from discussion by the Group. If a representative test sample of insignificant size can be taken from one specimen or a collection of specimens then any destructive test on the sample should be accepted as a legitimate "non-destructive" test of the specimen or group of specimens as a whole.

If that is the present accepted position, what is or is not a subject for discussion by the Non-Destructive Testing Group still remains partially undefined. There are dangers in too wide as in too narrow an interpretation. By the bulk of the Group's interests we take it that a "non-destructive" test must fulfil the following criteria:

(i) A physical measurement on a material must be involved.

(ii) The method must be either strictly non-destructive or easily applicable to small portions of a specimen or group of similar specimens.

(iii) The results must tend to depend sensitively on small changes in specimen formation, production or uncompleted service.

(iv) The purpose of examination must be to relate past history with the future service performance to be expected from a particular specimen or group of specimens. (Note that only by this criterion are most technological and research investigations into the usefulness of certain compounds, mixtures, alloys, etc., excluded.)

Conventional X-ray diffraction methods in non-destructive testing

Having so defined non-destructive testing we see that X-ray diffraction investigations[1] almost invariably fulfil conditions (i) to (iii):

(i) A physical test of matter is involved.

(ii) The method is non-destructive in the sense that the physical and chemical properties of the sample are unchanged. Admittedly there are such questions as radiation damage (in the widest sense of the term) which even at the highest quantum energies employed for X-ray diffraction is normally quite negligible. The formation of colour-centres in certain ionically bound materials is an interesting exception. Soft X-rays are thus destructive of the colour-free transparency of common soda-lime glass.[2] One might also cite the example of electrical conductivity which in some specimens would be temporarily changed. None, however, on the score of such exceptions, challenges the right of this Group to discuss radiography; and X-ray diffraction studies in this sense are easier to justify.

The non-destructive investigation of large specimens by X-ray diffraction may cause difficulties but these are in the first place just a matter of design of suitable

equipment. There is really nothing to prevent the building of small or, at any rate, mobile X-ray tubes and cameras to record all but small-angle diffractions from specimens larger than could be radiographed, if this might once more be used as yardstick.

(iii) X-ray diffraction, depending on the inter-atomic configurations sensitively depends on changes in specimen formation or production and can be influenced by severe service conditions.

It is only the fourth criterion that much X-ray diffraction work fails to satisfy. Much of crystallography is concerned with atomic structure analysis for the determination of bond-lengths and molecular configurations which are fundamental characteristics of the elements, compounds, or alloys concerned, without involving service performance of individual specimens. The same probably applies to much X-ray identification work. If an organic chemist asks whether a synthesized sample is identical with a reference compound, if a quarry manager wonders whether a given rock contains a certain mineral or if a plant metallurgist wishes to know the origin of a non-metallic inclusion, X-ray diffraction can probably provide the answer without destroying the sample submitted, but it would be stretching the definition too far to say that these are non-destructive tests within the meaning which the Group ought to have in mind.

There are, nevertheless, important non-destructive X-ray diffraction tests which suggest themselves, and which industry has begun to use. It is certain that in future they will have a vital part to play in all branches of industry. They fall into five main types of test,[1] any one of which is worthy of a fuller treatment than can here be given:

(i) No one doubts that industry will tend more and more to measure automatically and almost continuously the chemical composition of its products, raw materials and intermediates by purely physical methods. While one must applaud the impressive successes of ultra-violet and mass spectrometric equipments, X-ray fluorescence spectrometry will also have a significant part to play. For elements of atomic number greater than about 12, the X-ray method is most promising because of:

(*a*) the simplicity of the spectra,

(*b*) the uniform excitation of the spectra of these elements.

(ii) The importance of X-ray "fingerprint" identification or quantitative phase analysis by X-ray diffractometry might perhaps be illustrated by an example from the steel industry. The manufacturing difficulties of many very hard steels, such as some tool and ball-bearing steels, centre around the prevention of more than traces of austenite being retained in the final product. How could one manufacturer with but conventional methods compete with another to whose production management's notice is brought continually the austenite content in the product? In this example and for many similar ones X-ray diffraction methods are without rival at present.

(iii) Orientation textures result from most natural and industrial processes and they influence most physical properties especially of materials with strongly anisotropic crystal structures. The determination of a single complete orientation texture as illustrated conveniently and conventionally by a pole figure is necessarily laborious. In framing non-destructive tests, therefore, much scope is offered and ingenuity needed for devising empirical measurements relating to only a fraction of the full pole-figure information, but aptly fitting the characteristics of the material and the manufacturing process involved.

(iv) Changes in lattice parameters which can usually be measured with very great accuracy can sometimes be interpreted in terms of solid solution, temperature or lattice-strain effects. The last due to "locked-in" stresses are practically the most interesting and have been used successfully for the non-destructive testing of some non-ferrous alloys. For many alloys, notably steels, the effects are probably too close to the lower limit of detection to provide a basis for promising non-destructive testing procedures.

(v) Changes in sharpness of X-ray diffraction maxima may be due to an even greater variety of causes. Some of these, at least in theory, can be distinguished by the kind and variations of distortions shown by different X-ray reflexions. Where crystal-size effects are chiefly responsible the interpretation may be simple such as in the testing of some industrial catalysts. Often, however, this type of test must be applied empirically, without distinction being made between the effects due to crystal size and those caused by crystal strains.

So here then are five distinct X-ray diffraction methods of non-destructive testing, each of very great promise and each based on theoretically well-founded and laboratory-proved methods. Yet one must face the fact that industry appears to have made but very little use of any of these methods when compared with their potentialities as they appear at first sight.

LIMITATIONS OF CONVENTIONAL X-RAY DIFFRACTION PROCEDURES

A close scrutiny of the reasons (over and above the natural reluctance against adopting new methods of technological control) leads us to believe that there are only two real obstacles to the far wider use of X-ray diffraction methods in non-destructive testing.

Firstly, there is the small size of the volume of a specimen which can be readily examined. In pointing this out we do not merely refer to the small sample size—a 10^{-6} g sample has been investigated, 10^{-3} g of any material is quite conveniently handled and more than 1 g of sample is usually an embarrassment. The consequences of these facts can often be overcome by careful sampling techniques, although even they fail when one is required to pick a representative gramme from a truck-load of raw material. The real difficulties lie in the inability of the relatively long "characteristic" X-rays to penetrate below the surface layers of a specimen. This is illustrated by a plot of the log half-value layers (h.v.l.) of steel for different wavelengths (Fig. 1). The accuracy of the data for short wavelengths is in doubt,[3] but we are only concerned with orders of magnitude. Furthermore, the h.v.l. method of presenting the data is out of fashion but, as is easily visualized, it gives the order of layer thickness from which X-ray diffraction can be expected to be recorded. Assuming normal incidence and emergence even, diffraction from any deeper material is reduced by a factor of more than 4 as compared with diffraction from the true surface layer. For the usual cobalt radiation this half-value layer is 1/2000 in. For X-ray tests the surface condition and treatment of a sample is thus a research problem. No universal

procedure for surface treatment prior to test has been or is likely to be found such that results representative of the bulk are obtained.[4]

One may well argue that this difficulty is not new to metallurgy and the mineralogy of opaque ore minerals. Exactly similar observations could be made on classical microscopic methods. Indeed, the parallel is probably even closer; for is this not one of the reasons why micro-examination, perhaps the most powerful metallurgical method of inspection used in the research laboratory, finds few outlets in non-destructive testing technology?

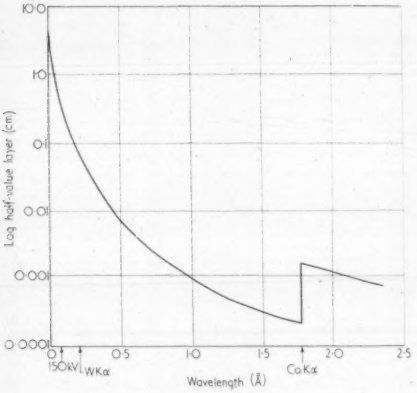


Fig. 1. Half-value layers for iron

Secondly, many of the properties that really matter, that make the difference between good and bad service performance, are neither simply dependent on the phases present nor on their bulk characteristics. What the user of a creep-resisting steel, for instance, wishes to know is not merely that say κ-carbide is present but whether it is present as an exceedingly fine precipitate on slip bands. This is incidentally why the carbide detection in such samples is so difficult and why the unfortunate steelmaker must work in very narrow composition and heat-treatment ranges close to ominous phase-boundaries.

Allow another example to be given: the observed tensile strength of metals, which after all is one of their most important properties, is far less than the one calculated on the basis of perfect metal-atom lattices. It is clear that the correct explanation of the observed facts can only be found in terms of some lattice defects such as the imperfections that are normally called dislocations. Maybe those dislocation experts are right who believe that a grain is in danger of being cracked in a certain manner only when like dislocations are piled up along slip planes near the grain-boundaries there to form a purely local weakness resembling a Griffiths' micro-crack. X-ray diffraction observations yielding information averaged over a far greater bulk are not sensitive to the local effects of such piled-up dislocations. Polygonization, the effect due to the slight interlattice angle of the grain portions which the dislocations separate, might be picked up in a crystallographic laboratory experiment but the effect is too small to be promising as a non-destructive test.

In crystallographic research generally, interest is shifting to some extent from investigation of perfect structures to that of crystal imperfections. Generally speaking that change of outlook involves great refinements in technique which cannot be readily contemplated for technological tests, although in these imperfections lie some of the explanations to the technologically most significant properties of materials.

HIGH-VOLTAGE X-RAY DIFFRACTION IN NON-DESTRUCTIVE TESTING

The potentialities and limitations of non-destructive testing by conventional X-ray diffraction procedures have now been discussed briefly and it remains to venture our opinions on what contributions, if any, high voltage X-ray diffraction work might make. Although we judge them to be modest, the prevailing opinion that the coherent scattering cross-section for wavelengths less than about 0·5 Å is too small for all practical purposes must be modified. It must, however, be remembered that the great majority of useful diffraction pictures are taken with approximately monochromatic X-rays, whereas at high voltages there are at present no good monochromatic sources of radiation. Although some rather weak, monochromatic high voltage X-ray beams have been produced we have not so far taken X-ray diffraction pictures with them and do not think that their practical use is at present promising. One is thus limited to polychromatic high voltage X-ray pictures such as those recently described by us;[5] so that the technique is applicable only to rather coarse-grained samples (grain diameter greater than about $\frac{1}{2}$ mm).

Originally we intended merely to study diffraction mottling in radiography. Though it was in its essentials correctly described and interpreted by Glaisher, Betteridge and Eborall,[6] it appeared to us an unexpected and partially unexplained phenomenon. To the physicist it is relatively immaterial whether or not the mottle interferes significantly with radiography. For a fuller understanding we therefore set out to isolate the diffraction effects from the ordinary radiographic image. As soon as one cannot assume rectilinear propagation from source to film one is ignorant of the path of a ray that has reached the film at a certain spot unless one collimates the primary beam to permit but one path from source to specimen. This reasoning leads directly to high voltage Laue type photographs.[5] This study has helped us a little in controlling diffraction mottling effects in radiography, but a greater prize would be the gain of a new method of non-destructive study of some materials.

We have explained the typical appearance of high voltage X-ray photographs [see Fig. 4(*b*)] in terms of polychromatic streaks due to the finite reciprocal spot size.[5] The departure from ideally perfect crystals with infinitely small reciprocal spots does not have to be great for Laue spots to be smeared into such streaks. Purely elastic lattice strains giving distortion of reciprocal lattice points parallel to the origin vector cannot be responsible, but polygonization producing extension of the reciprocal spots perpendicular to the origin vector could produce the observed streaks.

With slightly more refined equipment (Fig. 2) and with growing experience we have now found that there are two other types of high voltage X-ray photographs produced by some specimens. These differ essentially from the one type previously described but in practice gradations are found between all three types.

One of the new types can be described as a true high voltage Laue picture in which the spots are sharp produced by very small reciprocal lattice points and therefore very perfect

crystals. In the example shown (Fig. 3) the identical sample area was photographed at 120 and 160 kVp, the latter showing additional spots. This type of picture can be obtained from portions of numerous precision-cast high alloy steel specimens with compositions having a fairly narrow liquidus/solidus interval.

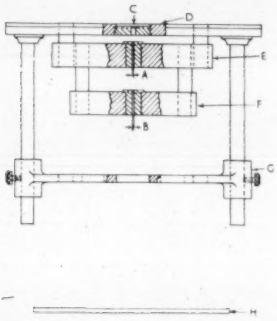
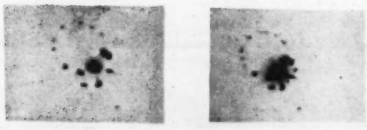


Fig. 2. High voltage diffraction apparatus

C, X-ray beam; *D*, beam-limiting aperture; *E*, primary collimator; *F*, scatter-guard slit; *G*, specimen holder; *H*, photographic film at variable distance from specimen.

Interchangeable bushes

	A diam. (in.)	*B diam.* (in.)
fine	0.020	0.025
medium	0.040	0.050
large	0.081	0.099



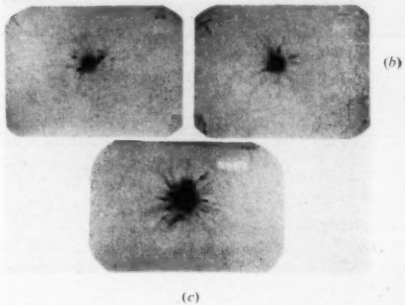
(*a*) (*b*)

Fig. 3. High voltage Laue pictures

(*a*) 120 kVp; (*b*) 160 kVp.

The third type of high voltage X-ray picture [Fig. 4(*c*)] depends on some unfiltered characteristic radiation (as a rule tungsten for standard radiographic tubes) giving vestiges of Debye–Scherrer rings when the sample contains at least some grains below the size limit quoted. The effect is best understood by reference to Fig. 1. The half-value layer for WKα radiation does not differ by more than a factor of 2 or 3 from that at the white radiation peak. The intensity/wavelength curve for the primary beam has such a very high narrow peak at the characteristic wavelength that even after considerable filtration it remains the most important wavelength for diffraction effects although the total energy is far greater in the white band which therefore largely determines the normal radiographic appearance.

The appearance of the three different types of crystal is surprising perhaps in different areas of one and the same precision-cast turbine blade (Fig. 4). It is inconceivable that these three areas could have identical physical characteristics. This implies that such specimens could never be represented by one mechanical testpiece. The three areas differ in apparent grain size having 9, 30 and 135 grains per arbitrary unit area respectively. An X-ray count[1] in the same areas



(*a*) (*b*)

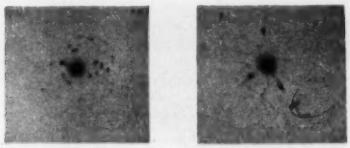
(*c*)

Fig. 4. Three high voltage pictures of different areas of same precision-cast turbine blade (alloy steel, 23% chromium, 12% nickel, 3% tungsten, 2% silicon, 0·2% carbon)

(*a*) true Laue spots; (*b*) polychromatic streaks; (*c*) concentration of spots on Debye–Scherrer ring.

suggests a ratio of 9 : 25 : 39 crystals per unit volume. These observations are in good agreement if one allows for the fact that the smallest crystals are missed by the X-ray diffraction method. Thus there is hope of devising a non-destructive X-ray grain-size test. In practice it must be remembered, of course, that in the example quoted the different quality of grains is probably more significant than their size difference.

It is inconceivable to us that fatigue effects could leave unaffected the perfection of the crystals, giving true high voltage Laue photographs. Fig. 5 illustrates the X-ray



(*a*) (*b*)

Fig. 5. High voltage pictures of fatigue specimen (alloy steel, 11% chromium, 35% nickel, 1·6% manganese, 0·9% silicon, 0·35% carbon)

(*a*) unfatigued; (*b*) fatigued.

pictures obtained from a specimen one end of which was given 20 million stress reversals at 22 t/in.^{2}. The X-ray picture of the fatigued end [Fig. 5(*b*)] is of the polychromatic

streak type as might be expected had polygonization occurred, while the picture from the unfatigued end [Fig. 5(*a*)] shows no such effect. We therefore follow Franks and Holden[7] who have observed small angle diffractions with normal wavelengths in rejecting accepted opinion by claiming that fatigue is at least in some cases accompanied by a measurable change in X-ray diagram.

Most of the experimental work described in the latter part of this paper has been carried out by Mr. B. Newboult. The authors wish to thank Mr. E. W. Colbeck, Metallurgical Director of Messrs. Hadfields Ltd., for permission to publish this communication.

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Symposium on principles of penetrant methods

In Paper 1 Mr. Carson discusses the advantages and disadvantages of penetrant methods of crack detection compared with magnetic methods for ferromagnetic material. He concludes that fluorescent methods are more satisfactory than penetrants employing a dye and he gives a summary of the views of a Panel of the British Welding Research Association.

Mr. Cook poses eleven questions in Paper 2 as a framework for research towards ascertaining what the underlying physical principles are that make crack detection by penetrants successful.

In Paper 3 Dr. Schnurmann discusses the three different types of fluorescent inks used according to their physical action, and follows this with a brief discussion of the dye penetrant method. He concludes that the selection of the most efficient penetrant method must be made on empirical grounds for any particular instance.

These opening papers are followed by a report of the discussion on them.

Paper 1. By H. L. CARSON, B.Sc., A.Inst.P., British Welding Research Association, Abington, Cambridge.

While it is agreed that magnetic methods are the most sensitive for the examination of ferro-magnetic materials there are occasions when they cannot be used and it is then desirable to employ penetrant methods to inspect magnetic steel specimens for surface defects. The penetrant method, unlike the magnetic method, is restricted to defects which are actually in the surface of the material, or which have a channel opening on to the surface. Cracks are the most important defects in any specimen, and it is imperative that a penetrant method of defect detection should be capable of revealing every surface crack which exists.

These cracks can be classified into two general types:

(1) impermeable cracks,
(2) permeable cracks.

Impermeable cracks. These fall into four classes:

(*a*) "Tight" cracks where the sides are in close contact due to internal stresses bringing the sides together, and absence of foreign matter to keep them apart.
(*b*) Cracks completely sealed with products of corrosion, or oxidation, which may occupy a greater volume than the metal from which they were formed.
(*c*) Cracks to which a dye penetrant has previously been applied and which have been sealed up by it.
(*d*) Cracks which have been "peened-over" by the action of machining.

Permeable cracks. These may be classified under three headings:

(*a*) Cracks which are open due to distortion of the material during fabrication.
(*b*) Cracks which are kept open by stress.
(*c*) Cracks which are propped open by foreign matter which does not seal the cracks.

While both impermeable and permeable cracks in ferro-magnetic materials can be readily found by magnetic methods, only cracks of the permeable type are likely to be found by penetrants. However, even in these cases it is imperative that the surface of the material should be clean and thoroughly degreased. Again, the presence of roughness or scale on the surface can render it impossible for all traces of a dye penetrant to be removed. Under these conditions it is difficult to detect a fine crack against a pinkish background.

In some practical investigations which were conducted on a fatigue crack in the weld of a butt-welded pipe, it was found that the crack could be readily revealed by magnetic particles and appeared rather like a scribed line. Penetrant methods, however, completely failed to reveal this crack, even though it penetrated through the entire thickness of the material. This may, of course, have been due to the crack being filled up by the prior application of magnetic particles. On the other hand, some very fine cracks in ferro-magnetic materials have been found by penetrants. It is anomalies of this nature which require to be explained.

The above discrepancies all relate to tests on ferro-magnetic materials and it seems possible that the presence of rust may play a part in making detection difficult. While it appears to be easier to detect defects in non-ferrous materials by penetrants, no check for other defects is possible by magnetic methods. Hence the same comparison conditions are not possible.

Of the two general types of penetrant available, using dye or fluorescent material, it appears that the fluorescent method represents a more satisfactory and sensitive test.

A fluorescent penetrant can be used to give clear results on a reasonably rough surface and it does not appear to leave a residue which clogs defects and prevents subsequent applications from penetrating. The sharp green indications under ultra-violet light are much easier to see, possibly because the eye is more sensitive to the green end of the spectrum than the red. The red dye method does not require the provision of semi-dark viewing condition, as does the fluorescent method, and the size of the blot round the edges of the defect gives a rough measure of the volume of the defect. However, some red dyes do clog defects and render them undetectable and the poor contrast between the dye indication and the background are serious limitations of the method.

There is one final point. Certain penetrants of both fluorescent and dye types are water washable, whereas others are not and require the use of an emulsifying agent. There appears to be some evidence to suggest that more efficient penetrant action is associated with those penetrants which are not water washable.

To conclude, the following is a summary of the views of the Magnetic and Penetrant Methods Panel of the British Welding Research Association on the present state of penetrant methods of inspection.

(*a*) With ferro-magnetic materials, much better results are usually obtained with magnetic methods than with penetrant methods. When, however, the magnetic method is not applicable, useful results can often be obtained with penetrants.
(*b*) Once certain dye penetrants have been applied to a

specimen, they cannot be completely removed by normal cleaning methods. As a consequence, it may be impossible to reveal defects by subsequent penetrant tests.

(*c*) Fluorescent penetrants do not appear to clog defects and render them undetectable by subsequent penetrant applications. However, the fluorescence is influenced by contamination and may be rendered ineffective by the presence of oil.

(*d*) The volume of a defect into which a penetrant has entered determines the magnitude of the indication produced. In the case of a dye penetrant, defects of considerable magnitude may result in the surface indications being blurred and confused.

(*e*) Small defects which are just visible to the eye with the aid of a magnifying glass are the ones best suited to detection by a penetrant.

(*f*) It is difficult to assess the relative sensitivities of dye penetrants since tests on the same specimen cannot, in general, be made with several dye penetrants. A means of overcoming this difficulty would make penetrant assessment more positive.

(*g*) In cases where penetrants have to be used, a knowledge of the fabrication process and the type of defect likely to be encountered is necessary as an aid to interpretation.

(*h*) The physics of penetrant action is not clearly understood and work of a fundamental nature on this aspect of the subject is necessary.

Paper 2. By W. G. Cook, B.Sc., Rolls Royce Ltd., Derby.

The past two years have seen a very encouraging increase in interest in new methods of non-destructive testing and these have been very marked in the field of inspection by penetrant methods. These methods using liquids, when properly applied, are a valuable visual aid and the practising engineer is today faced with an almost embarrassing range from which to choose, both in the red dyed and the fluorescent varieties. To assess them objectively is an even greater embarrassment, particularly on aero engine work, where the standards of crack detection are very exacting.

On a first approach to this problem one is struck by the meagre nature of published scientific information and the elementary errors perpetuated in such explanations as statements to the effect that heat expands a crack and draws in the penetrant and cooling makes it contract to expel the liquid.

To assess the various penetrants available, two main lines of attack suggest themselves. The first is to carry out field trials. The use of isolated specimens can be very misleading and a proper assessment involves quite a considerable programme of testing. Numerous other variables, apart from the penetrants themselves, are encountered and an objective assessment is well nigh impossible. Nevertheless, a great deal of work has been carried out on this basis and a broad idea of the relative merits of the various products has been gained. Details of this work are not relevant to the purpose of this paper.

The second approach is to determine the physical properties which are inherent in a good penetrant and, if possible, devise standard tests for these properties. This will give a three-fold reward—first, to enable the penetrants to be classified in order of penetrating power; second, to enable a specification to be drawn up and, third, to enable objective routine control tests to be carried out. It was with this aim in view that we turned to the work of the physicist but could find little evidence of any efforts in this field, and it is therefore with a hope of filling this gap that the following questions have been formulated:

(1) What is the mechanism by which penetrating fluids enter blind cracks in metals? Is it capillarity, spreading, or both? Does vapour pressure play a part? What part does the trapped gas play in the crack?

(2) What physical properties make for a good penetrant? Surface energy, viscosity and polar properties seem likely to be involved but there may be others. Does the free surface energy of the metal at the crack play a part?

(3) The performance of the penetrant is often improved by heat. What precisely is the effect of heat?

(4) Do the conditions apply to all metals or are there likely to be specific relationships? What is the effect of the surface condition of the metal in a crack?

(5) Are there likely to be new chemicals with more pronounced penetrating powers?

(6) Is vibration likely to be beneficial?

(7) After the penetrant has entered the crack, the surplus fluid is removed from the surface by a number of techniques, the commonest being water washing or emulsifying followed by water washing. In some cases organic solvents are used. Such a compound must be an effective cleaner but not remove the penetrant from cracks. This leads to the need of a liquid with good cleaning powers but poor penetrating powers. What are the ideal properties of such a fluid in terms of measurable physical properties?

(8) After cleaning and drying, the penetrant either seeps from the crack or (more commonly) is drawn out by an inert powder, applied either dry or in the form of a suspension in a volatile carrier. What is mechanism of the drawing out? Will grain size and grain form play an important part?

(9) The crack is then seen by the contrast between the penetrant drawn from the crack and the background. The two commonest are a red stain against a white background and a yellow or green fluorescence against a purple background. What is the ideal contrast of signal to background?

(10) Are there any new super-fluorescents or materials likely to give improved contrast?

(11) The final question should perhaps have been asked first, since the primary requisite is effective cleaning. What are the physics of vapour degreasing in (say) trichlorethylene?

These questions are merely intended to form a framework since it is realized there may be physical properties involved other than those mentioned. However, some of them may serve as a starting point.

Paper 3. By R. Schnurmann, M.Sc., F.Inst.P., Manchester Oil Refinery Ltd., Manchester.

In nearly every industrial field the demand exists for simple and inexpensive, speedy and yet reliable means of flaw detection to ensure the soundness of structural components and to increase safety margins. For the examination of

magnetizable materials the magnetic particle method is a very sensitive tool, whereas for non-magnetizable materials methods must be used that rely either on the reflexion of waves from the boundaries of a crack or on the actual permeation or partial impregnation of a crack by a suitable liquid. The oldest of these "penetrant" methods is the "hot oil and chalk method." This, however, is tedious and does not give good contrast since the oil spreads in the chalk layer.

Modern penetrant methods are based on two very simple principles. One is that the penetrant deposits a fluorescent material which enhances the contrast of the otherwise indiscernible crack and thus makes it visible to the naked eye, and the other depends on the spreading of a liquid from the defects. The selection of the appropriate penetrant method is a matter of experience, judgement, and expediency. In some cases speed and simplicity of application are more important than the spotting of minute flaws. In others it is vital to be certain that even a minute defect will not be missed. The inspecting personnel is faced with the difficult task of deciding where to draw the line between a skin defect and a crack which is deeper than it is wide.

The two groups of penetrants in use now are fluorescent inks and dye penetrants. By the nature of their physical action there are three different types of fluorescent inks:

(1) The simplest one to use is a non-fluorescing liquid which when applied to a solid surface dries very quickly and leaves on the impregnated surface a deposit which fluoresces vividly in "ultra-violet light" (i.e. a light source from which visible light has been filtered, as otherwise the fluorescent indication is swamped by it). Owing to its penetrating properties this "ink" reveals almost instantaneously cracks and pores which extend through the thickness of, say, a welded or riveted component when a drop of the "ink" is brought on to one face and the opposite face is viewed with "ultra-violet light." On the other hand, though, when the impregnated surface is viewed under "ultra-violet light," large cracks and porous areas stand out from the fluorescing background by their more intense luminescence, finer defects only become apparent when the fluorescent background has been washed off. This "fluorescent dry deposit method" distinguishes itself by its simplicity, and by the speed with which results are obtained; it is the one penetrant method which gives a true delineation of defects in all materials barring those of a spongy texture. With testpieces of closely knit structure its application is restricted to the detection of defects of a size which with the enhanced contrast provided by the deposited fluorescent material can be picked out with the naked eye.

(2) When the defects are so small that an enlarged indication is required for visual inspection either the "wet solution method" or a fluorescent adaptation of the "chalk adhesion process" must be used. With the former the testpiece is impregnated with a solution of a fluorescent material. The treated surface is then flushed with a detergent and hosed with water to remove redundant material. After drying of the surface the liquid which became entrapped spreads from existing defects. The solution itself does not fluoresce and therefore time must be allowed for the fluorescent material to form a supersaturated skin which will fluoresce under "ultra-violet light." This method gives an enlarged outline of the defects.

(3) The fluorescent adaptation of the "chalk adhesion method" also acts as an "enlarger." It makes use of a brightly fluorescing comparatively viscous liquid. After an empirically determined impregnation time the surface is flushed with a detergent solution and hosed with water. When dry, a non-fluorescent powder is dusted on that will adhere to existing defects by exerting a mild blotting action on the entrapped liquid. The redundant powder can be blown off, and white ridges of adhering powder can be seen in ordinary light, but they are seen much more strikingly under "ultra-violet light" by their very brilliant fluorescence.

There may be occasions when the use of "ultra-violet light" is not convenient or not advisable and when the application of dye penetrants is preferable. These are solutions of a bright red dye in a liquid of good wetting properties for metals, plastics, ceramics, and glass. The redundant dye solution must be removed from the impregnated surface either with kerosene or water. Usually a "liquid developer" is used to produce the flaw indications. This quickly forms a dry white coating of uniform porosity that acts like blotting paper on dye solution which had been entrapped in the defects during the impregnation period. The result of the "developing" process is a red flaw indication on a white background. Another developing method involves a plastic film coating of the impregnated testpiece. This can be peeled off with a transfer of the flaw indication (Fig. 1).

Fig. 1. Transfer of a flaw indication with a dye penetrant. The impregnated testpiece had been coated with a solution of cellulose acetate. During the setting of the film the crack indication appeared. The film was then peeled off

All penetrants for non-destructive testing must seek and enter into defects in order to be able to show their presence and location. Nevertheless, the name "penetrant" is a little misleading for these fluorescent inks and dye penetrants since not all of them have good penetration properties. Indeed, with the fluorescent adaptation of the "chalk adhesion method" described above, good results are obtained in the detection of very fine cracks although the liquids employed are very sluggish penetrants. The surface tension has little effect upon the sensitivity of these flaw detection media, whereas their viscosity should be adapted to each particular type of application. It is important that they should be capable of wetting different types of surface.

For the "fluorescent dry deposit" method it is essential to use a low viscosity fluid of high volatility. This must carry in solution as high a concentration as possible of a powerful fluorescent material. High fluidity coupled with good wetting properties will make the "ink" surge through defects which extend throughout the thickness of the material, whereas in the case of cracks and porosity of limited depth some of the entrapped air may become dissolved and some will force its way past the penetrating liquid.

With the "wet solution method" on the other hand, a carrier of low volatility and very good wetting properties is required for the fluorescent material. Low volatility means higher viscosity so that longer impregnation times are

required of the order of minutes. Even more time may elapse for the liquid to re-emerge from the defects, spread and eventually exhibit fluorescence.

In the fluorescent adaptation of the "chalk adhesion method" use is made of a brightly fluorescing solution of appreciable viscosity. It will thus stay put in the defect during cleaning of the impregnated surface and does not emerge by itself. To withdraw it from defects a powder of suitably selected particle size and shape must be applied.

The carrier medium must have a high degree of solubility for the dye and must be of such a nature that a thin film of dye solution does not dry, yet does not spread excessively in the "developer" coating.

Cracks must be free from oil, grease, or mechanical debris to allow penetrants to enter into them. The use of more than one penetrant method can give complementary results. Fig. 2 shows a crack in a brazed tool bit with the "wet solution method" (on the left) and with a dye penetrant (on the right).

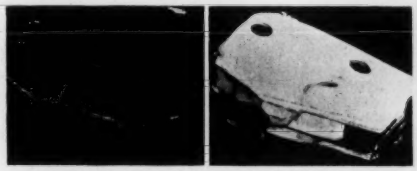

Fig. 2. Similar *S*-shaped cracked indications on the same brazed toolbit by the "wet solution method" (on the left) and with a dye penetrant (on the right). The "wet solution method" indicates that the crack becomes narrower towards the top of the *S* where the larger spreading of the dye solution shows greater depth

The most difficult problem that can arise in non-destructive testing is that of deciding whether or not a flaw indication reveals a crack. There are borderline cases, which fortunately arise very rarely, when different methods appear to give conflicting evidence. For example, observations were made on a forging and it was found that the "fluorescent dry deposit method" gave no indication which was visible to the naked eye, whereas all penetrant methods which involved spreading of the indicating liquid gave an indication that might well be interpreted as showing a crack. However, when in this case the "dry deposit method" was used and a photograph taken, the photographic plate showed a few spots of deposited fluorescent material giving the impression of a slag line, whereas with the other methods the picture of a crack was simulated owing to the spreading properties of the indicating materials. Similarly, with a strip containing very narrow artificial cracks no visible indications could be produced with the "fluorescent dry deposit method" although the fluorescent solution was sufficiently searching to enter these cracks. This was again proved by means of photographic inspection (Fig. 3).

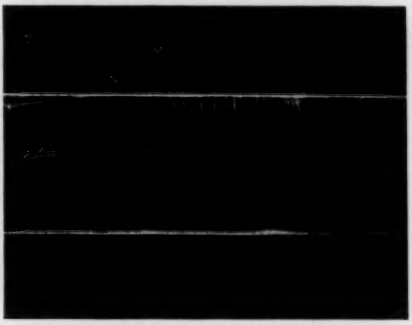

Fig. 3. With an exposure time of thirty minutes a photographic plate reveals these crack indications by the "fluorescent dry deposit method," whereas the other methods which lend an enlarged outline to defects make them visible to the naked eye

Physical principles involved in the formulation of penetrants for flaw detection are very simple. The selection of the most efficient penetrant method must be made on empirical grounds for any particular inspection problem. It appears, however, that there is no single method which will answer all practical requirements and the complementary value of the various penetrant methods must be considered. Thus it may sometimes be an advantage to have indications which give an enlarged outline to existing defects, whilst in other cases it may be necessary to indicate the true outline of a fault.

DISCUSSION

Sir Eric Rideal (Chemistry Department, Imperial College, South Kensington, London): I have had a lot of letters sent to me which I have read through and have tried to understand exactly the problems that they raise. I thought I could not do better than mention one or two of the points. They may be well known to all of you, and if they are I would apologize. But these points have been raised in the form of questions by previous contributors so I thought I might attempt to answer them.

How rapidly does a liquid go along a crack or capillary? Many years ago I worked that out. It is rather complicated to consider all the factors involved, e.g. inertia and the like, but we can show that a close approximation is given by the expression

$$l^2 = t\gamma \frac{\cos\theta}{2\eta} \qquad (1)$$

where l = length in capillary penetrated in time t
t = time in seconds
θ = contact angle
η = viscosity
γ = surface tension

I obtained the following values:

	Penetration calculated	*Coefficient observed*
Water	11·31	11·40
Benzene	8·90	9·90
Ethylalcohol	5·35	5·65
Isobutylalcohol	3·75	3·7

If you are going to use a liquid for carrying a fluorescent material you should use something with a high penetration coefficient. The crack may run right through and then you

can get the time of passage but usually the crack only goes down a certain distance. On entry of the liquid the trapped air starts to compress, and as far as I can understand, nobody seems to have gone into that particular phase of the business. What happens to this air? I do not know. But one can see, first of all, that the pressure that is developed in that compressed gas must be higher than that outside. How much pressure is developed in a circular tube? This is given by the equation

$$\Delta p = 2\gamma/r \qquad (2)$$

Thus for micro-cracks, e.g. $r = 10^{-5}$ mm, the gas is under quite a high pressure, and it must start to dissolve in the liquid. How quickly does this gas dissolve? I do not know of anybody who has answered this, but diffusive processes are by no means instantaneous. That is the first point I wanted to make. Now I will deal with the second one. There has been a good deal of discussion on fluorescent materials and dyestuff materials. But supposing your crack is closed at its extremity? It may start with what is termed a visible crack under a microscope, e.g. 10^{-4} cm, and gradually taper off to 10^{-7} cm. From the point of view of strength of materials, one has got to go down to a thickness of that order, where you get to the attractive portion of the potential curve.

These fluorescent molecules are big and so are the dyestuffs, e.g. 10^{-5} to 10^{-6} cm, so that they will not penetrate to the bottom of the crack. It is a convenient method, but it will not tell you about the baby cracks. But if these small cracks affect the strength of the material, they are important. You cannot see them, and if you want to do that, then one of the most convenient methods would be to use radio elements. For example with silver/copper/lead, you put silver into radioactive silver nitrate and an exchange takes place. The difficulty inherent in this method is as follows. It would be very convenient if you had a piece of silver and a silver atom came off this surface and exchanged with a radio ion, but unfortunately the atoms in the metal are all moving about inside and the result is that in time some of the radio atoms go inside the metal and, if we wait long enough, e.g. about 1 million years, the whole of the silver rod gets equilibriated with the radio ions. It would mean that if you are going to use the radio method by travelling over the surface with a Geiger counter, you have to do some sort of calibration. One possibility is to contact the metal with the radio ions for a definite length of time, allowing us to get a certain depth of exchange. The other possibility is to use bigger radio molecules which are strongly adsorbed and which do not exchange, such as long chain acids, amines and the like, each of them with a polar group depending on the nature of the metal. These are just two or three of the points that I would like to make.

Another possible method is to set up an electrolytic cell by means of a wet swab. Many years ago when Dr. Bowden and I were interested in the specific surfaces of metals, we were studying the deposition of hydrogen on metals. You get a polarization curve, and the magnitude of the i, V curve does depend upon the specific surface of the metal. We can evaluate specific surface quite easily in this way. The chief trouble would be experimental and would depend on whether one could devise a mechanical method of travelling over the surface with an electrode of known area with cotton wool over it, and following the polarization curve as it travels. In order to obtain a definite rise in potential, it is necessary to put down very many more coulombs than are needed on a plane surface. In many cases, e.g. sand blasted surfaces, it would be something like two or three hundred times greater.

Dr. E. W. J. Mardles (Royal Aircraft Establishment, Farnborough): With regard to the set of questions brought forward by Mr. Cook, answers can be given to some of them. Vibratory conditions do assist the penetration of liquids into holes and crevices, the movement of bulk liquid across a surface appearing to be of a slip-stick character. With the aid of a microscope it can be seen that the spreading of a liquid from the periphery at the solid surface is by small tongues of liquid pushing beneath the meniscus, an action stimulated by vibration.

The presence of air gaps in a penetrating liquid column increases the resistance, a maximum being reached when the air gap is about two or three times the capillary diameter. This effect first discovered by Jamin[1] for water in glass tubes was not found by Smith and Crane[2] in clean glass tubes, but we have been able to measure a meniscus resistance up to several dynes/cm for all liquids examined in glass and other tubes, when scrupulously clean and both wet and dry.[3] Recessional flow is often rhythmic and its rate considerably less than that calculated from Poiseuille's law due to the contractile force and periodic rupture of the surface film behind the receding meniscus. The anomalies could not be explained by any difference between the advancing and receding contact angles. The penetration equation of Washburn,[4] Rideal,[5] and Peak and McLean,[6] which takes into account solely the capillary, viscous, gravitational and inertia forces, is not in close conformity with published flow results when small forces are prevalent, specific chemical effects (degree of wetting, adhesion, etc.) being important. The time-dependent specific effects observed by de Waele and myself are much in evidence with dispersions of finely divided solids and determine the thixotropy and other rheological properties of the dispersion.

Again, the Young–Dupré equation modified by Harkins, which equates the coefficient of spreading with the difference between the work of cohesion and work of adhesion, has led to no useful results. It has been found that the spreading of a liquid and its penetration are non-Newtonian and time-dependent while contact angles vary with the method of forming the pool, time of standing, vibration, etc., and the resistance to flow is not calculable from the cosine of the contact angle.

An important factor in the spreading of a liquid into crannies and holes is the conditioning of the surface ahead of the bulk liquid by the migration of liquid molecules beyond the periphery assisted sometimes by vapour deposition. Films are formed which are sometimes visible by suitable illumination and magnification; a dye technique is helpful in showing thin zones surrounding the periphery. Pools of oil become surrounded by a zone of thin oil sometimes visible and detectable by friction tests. These thin films appear to be an integral part of the pool meniscus and in an advanced stage show ridges and droplets.

The rate of film creep of several liquids over a variety of surfaces has been studied and it appears to be dependent on the relative specific nature of the liquid and surface.

An interesting feature of the penetration of liquids into cracks and holes of small dimensions is the filiform nature. With diameters and distances below 10 μ the liquid film has a specific surface several hundred times greater than the bulk liquid, and there is a tendency, in accord with the Gaussian principle of minimum area, for the liquid to decrease its surface area by any means possible; cavitation is one of these means.

Mr. A. de Waele (Gestetner Ltd.): It is possible that phenomena at interfaces of fine powders and fluids may show some analogy to those at metal-liquid interfaces. In dispersions of fine powders, e.g. carbon black (0·025 μ), in mineral oils, considerable friction is exhibited even when the concentration is well below that of close packing. The addition of a wetting agent such as oleic acid materially reduces the rigidity or interstitial friction of the dispersion, yet there still remains a stray field of force tending to bind the particles of solid together, since rapid sedimentation occurs when the dispersion is diluted with a solvent. Addition of a material pertaining to the class of long polymer molecules, e.g. polymerized or oxidized fatty oil, "cyclysed rubber," or the like, not only reduces subjective rigidity but apparently so reduces the stray field of cohesive force that colloidal solutions are obtained on dilution with a solvent. The permanence in a colloidal state is further increased if the dry powder be well wetted with a volatile solvent previous to the addition of mineral oil, or if the dispersion be subjected to a high vacuum.

Thus interstitial friction would appear to be reduced or eliminated by a combination of adequate wetting and simultaneous extinction of the stray field by a strongly adsorbed dispersator. I have discovered no specificity between the nature of the dispersate and the dispersator, which suggests that the action is that of colloidal protection.

The semi-rigid dispersion of black in mineral oil shows large flocculi when examined under the microscope, but when sheared between slide and cover slip it becomes temporarily deflocculated and optically void. Measurements of the rigidity of such a dispersion at increasing periods of rest after shear show progressive increases of rigidity with time of rest. Further, the electrical conductivity of the material grows with time of rest after shear. Both these effects suggest that on a fissure overlaid with a suspension of magnetic powder or a solution of an adsorbable indicator vibration may further assist penetration.

Dr. K. Weissenberg (Department of Colloid Science, University of Cambridge): To facilitate a study of the efficiency of penetrants, and of the mechanism of penetration into cracks, it is proposed to use a technique of testing which is based on a new method of producing periodically homogeneous patterns of cracks of different types in the material under investigation.[7] The method has not yet been fully worked out for crystalline substances, such as metals, but periodically homogeneous patterns of fatigue and rupture cracks have been obtained in a well-reproducible manner for many amorphous materials including plastics, dry powders, pastes, suspensions, etc. The method consists of depositing a thin layer of the material on a deformable substrate (e.g. on a sheet of natural or synthetic rubber) and then subjecting the substrate with the adherent layer of material to homogeneous strains of various kinds till cracks occur in the layer. The testing of penetrants can then be carried out and a better understanding of the mechanism of penetration can be achieved by using a monolayer technique (*viz.* radio-active tracer elements) developed by Dr. D. E. Beischer.[8]

Dr. W. H. Banks (Printing, Packaging and Allied Trades Research Association, Leatherhead): I too was privileged by a preview of the questions asked by Mr. Cook but since Sir Eric Rideal has so authoritatively dealt with them the only contribution I can make is perhaps a comment on the contact angle of penetrant liquids on metals. You will recall that the contact angle appeared in Sir Eric's penetration equation associated with the surface tension in $\gamma \cos \theta$, a parameter sometimes called the adhesion tension. We have studied the variation of the contact angle of oils on metals in presence of water for a range of metals, and for all those studied we find that they become increasingly oleophobic to pure paraffin during continued immersion under conditions where air is not excluded. The final order is:

zinc, aluminium, copper, nickel, chromium, platinum, gold, silver
→ increasingly oleophilic

For oils containing oleic acid, the behaviour is different. Zinc and copper behave initially as the other metals in becoming more oleophobic on continued contact with oil and water but this eventually gives place to a reverse trend to increasingly oleophilic behaviour.

The main difference from the studies with pure paraffin, however, is the final order after the major changes have taken place. This final order is as follows:

iron, platinum, chromium, aluminium, nickel, gold, copper, zinc
→ increasingly oleophilic

Here an order begins to emerge which we believe is related to the strength of the hydrated oxide of the metal and hence in its tendency to react with acidic constituents of the oil. Regarding the cleansing of metals with chlorinated hydrocarbons, I believe there is a danger with some metals of chemical reaction which may be important in crack detection.

I would like to draw your attention to the possible exploitation of electrographic methods of examining surfaces. Some excellent papers which are worthy of note are contained in *Symposium on rapid methods for identification of metals* A.S.T.M. special Technical Publication 98 (June 28, 1949).

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Magnetic properties and the structure of metals

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There are many physical properties which are important both from the theoretical and experimental points of view in the study of ferromagnetic metals and their alloys. Some of these are of a more fundamental nature and are related to field-independent characteristics such as saturation intensity and Curie point. They may also affect the behaviour of ferromagnetic materials in low fields. Others which are concerned primarily with such low field properties as permeability, magnetostriction, and domain structure will be dealt with. These relationships are examined in order to appreciate the extent to which magnetic properties can be used as a means of detecting variations in the structure and properties of magnetic materials. The report concludes with a consideration of newer developments in magnetism which may have application in future.

The purpose of this article is not to deal with the technology of flaw detection by magnetic methods, but rather to explore general relationships between magnetic and other physical properties. These are particularly directed towards those magnetic properties of one kind and another which might be used as an indication of variation in the composition and structure of materials and specimens under test. It must be emphasized that this choice may be regarded as somewhat arbitrary and does not necessarily preclude the application of other properties which have not received explicit mention.

The account is divided into three parts. First of all there is a brief survey of the field-independent properties of magnetic materials, largely because these are fundamental and essential to what follows, and then such few applications as may be possible. These properties are chiefly concerned with the magnetic saturation intensity and the Curie temperature. The next section deals with such low field properties as I think are most relevant to those who wish to apply them to non-destructive testing. The chief of these would appear to be permeability, domain structure, magnetostriction, strain, etc. The third and last section briefly touches on such recent developments as may in the future have some relevance in detecting variations in structure and properties of magnetic materials.

Consideration of fundamental properties

Our first concern should be the origin of the molecular field of Weiss, his empirical concept, which, supported as it is by a massive weight of experimental data, must have some theoretical basis. This was first explained by Heisenberg in terms of the quantum mechanical exchange forces acting between electrons in neighbouring atoms, though even after twenty-five years the sign of the inter-atomic exchange integral is still unsettled. But Bethe[1] has given us a schematic relationship between the ratio of the atomic separations to the radii of the d shells and the exchange energy. Slater[2] has shown that this ratio is larger for ferromagnetic elements than for the other elements and solid solutions of the transition series. The curve passes from the ferromagnetic to the non-ferromagnetic region near $R/r = 1{\cdot}5$ This relationship is of use in deciding whether alloys are likely to be ferromagnetic or not.

The most important of our basic properties is that of the saturation moment. Much work has been carried out on both the ferromagnetic elements and their alloys. At very low temperatures in a magnetic field, all the elementary magnets are alined; a simple calculation enables us to find the magnetic moment we may associate with each atom, and so correlate this with the basic unit of magnetic moment which, since it is directly proportional to the angular momentum, can be expressed in quantized units. We find that the number of parallel electron spins per atom for iron, nickel and cobalt are respectively 2·2, 1·7 and 0·6—non-integral numbers for the quantitative explanation of which there is even now no satisfactory answer. Nor do we find any enlightenment if we make paramagnetic measurements on these elements above their Curie temperatures, for no matter what coupling between the electron spins we may assume no agreement is possible. The solution of this discrepancy is no doubt to be found in the band shape and distribution of the d-electrons concerned. Some suggestions to surmount this difficulty have been made, such as subdivision of the d band, but as yet there is no generally acceptable solution. When we turn to the Curie temperatures there is no satisfactory quantitative explanation of the values for the three ferromagnetic elements, but the variations of both Curie temperature and saturation intensity of binary alloys can often be closely correlated with structural data, particularly if we confine ourselves to series of binar ferromagnetic solid solutions in which the proportion of the non-ferromagnetic element increases from zero. Thus increasing dilution of the pure ferromagnetic element produces a steady decrease in both saturation intensity and Curie temperature so long as the alloy remains in the single phase state. But at the solubility limit, when the second phase is, generally speaking, non-magnetic, the Curie temperature ceases to decrease with increased dilution, though its sharpness becomes less well defined. At the same time the saturation intensity will usually continue to fall off, but at a different rate from that in the solid solution. The Curie temperature and the structure change which causes a disappearance of the magnetization are not likely to be confused, for the former is temperature reversible whilst the latter is rarely, if ever, so. There are other structural changes which may manifest themselves by their magnetic behaviour in different states. For example, the coercive force of an unstrained solid solution, is usually quite low, whilst the permeability is of the same order of magnitude as the parent ferromagnetic element. With the appearance of a second phase, the coercive force usually tends to increase quite rapidly, whilst the permeability drops to a low value. The degree of order of a ferromagnetic alloy also influences both saturation intensity and Curie temperature. For the alloy Ni_3Fe, the saturation intensity at ambient temperatures and below is a few per cent greater for the ordered condition, whilst the Curie temperature would be two or three hundred degrees higher in the ordered state were it not for the fact that order begins to break down to about 600° C. The most striking example is probably to be found in the nickel–iron–aluminium system. An alloy containing 30% nickel, 40% aluminium and the rest iron has an ordered Curie temperature at over 600° C whilst the quenched (disordered) alloy Curie temperature is below

100° C. Phase changes may be reflected in profound differences in the magnitude of the magnetic saturation intensity. Thus an iron–chromium alloy (50%) in the sigma phase is virtually non-magnetic. Heating to 855° C produces no change in the magnetic properties whilst the effect of an increase of 15° C to 870° C is to raise the intensity to 260 units and the full change to 700 is accomplished by holding at about 900° C for a few minutes, thus showing the phase boundary to lie between about 850° C and 875° C. Such cases can be multiplied but there is no general rule possible and each alloy must be considered in the light of its own possible structures.

When we consider the quantitative effect on the saturation intensity of the dilution of ferromagnetic metals, we find that the relationships established vary according to the ferromagnetic element concerned. Of these, the most satisfactory is nickel, and it has been established by the experiments of Sadron[3] and others that the diminution of saturation intensity is directly proportional to the number of valency electrons (4*s*) of the added metal. Thus the substitution of one copper atom for a nickel atom is equivalent to adding one electron to the alloy. This finds its equilibrium position in one of the "holes" of the partially filled *d*-shell of the nickel atom rather than in the copper atom in which it originally existed. In this way the average moment decreases from 0·6 by one Bohr magneton for each copper atom added, becoming zero at 0° K for about 60% added copper. This decrease is twice as rapid for an atom with two valency electrons such as zinc, three times for aluminium and so on. In every case the moment becomes zero when all the "holes" in the *d*-shell are completely filled. This is a quite attractive and indeed satisfactory picture but its extension to the other two ferromagnetic elements is by no means so good. Whether cobalt behaves similarly is open to question, largely owing to a combination of technical difficulties and the few binary solid solutions available. Iron most certainly does not appear to follow the rule for nickel; and the added elements act as pure diluents with no difference in behaviour of atoms with different valencies. We in Sheffield have work in progress on binary solid solutions with other metals of all three ferromagnetic elements, and expect that some further evidence on this problem will emerge. One should note in passing that iron–carbon alloys fall outside this generalization since alone amongst the binary iron-alloys the carbon is interstitial. It is possible in the light of the above evidence to form a not unsatisfactory picture of the electron bands of the ferromagnetics and their filling up in solid solutions, though the clarity decreases as we pass from nickel through cobalt to iron, and the finer points of detail present some difficulty in interpretation.

During the last ten years another class of magnetic material has come into prominence, i.e. the ferrites. Whilst these materials come outside the definition of metals, they are "ferromagnetic" in behaviour. The prototypes have formulae of the type $MO \cdot Fe_2O_3$, where the three ions, the divalent M, and the two trivalent ferric ions are arranged such that the two latter are either parallel or antiparallel. Thus since the ferric ion has 5 holes and if we assume that the M ion has *m*, the magnetic moment corresponds to either 10-*m* or *m* spins according to which arrangement is followed. This gives entirely satisfactory agreement with experiment, and this is largely due to the fact that there are no conduction (*s*) electrons to introduce complications. This, of course, means that there is no source for eddy currents due to alternating fields, a factor which is in some measure responsible for the rapid technological developments of these materials.

The two foregoing properties of ferromagnetics can be regarded as the most fundamental. They do not depend upon the magnitude of an applied magnetic field and can be regarded as dependent only on the spontaneous magnetization, i.e. the domain magnetization appropriate to the temperature, but with the direction of magnetization differing from one place to another in the specimen under consideration. The two parameters we have dealt with above may be regarded as the maximum value of the domain magnetization, and the temperature at which it decreases to a zero value. Whilst these properties may only have indirect application to problems of magnetic testing, an appreciation of the impact of these data and their explanation is required in what follows.

LOW FIELD PROPERTIES

We consider now the significant low field properties, such as crystal structure, domain structure, effect of strain, etc., and all those factors which influence the permeability, and it is only in the last twenty or thirty years that we have been able to attempt any satisfying correlation. Probably the measurements of the directional properties of single crystals of the three ferromagnetic elements constitute a suitable starting point, for here is the one factor which has most effect upon the differences in magnetic properties. Single crystals of the ferromagnetics are more easily magnetized in some directions than in others, but here emerges one of the difficulties of generalizing for these three elements, for nickel with a face-centred cubic structure magnetizes most easily along the [111] axis, but iron, body-centred cubic in the ferromagnetic state, along the [100] direction, whilst the easy direction in close-packed hexagonal cobalt is normal to the hexagonal plane, all directions in this plane being exceedingly difficult to saturate. Several thousands of oersteds are required compared with about five hundred for the two cubic ferromagnetics. It is interesting to note that the measurements carried out on cobalt at higher temperatures where the hexagonal structure passes over to face-centred cubic, the directional properties closely resemble those of nickel. Thus it is evident that this crystalline anisotropy is a structure-sensitive factor rather than one that depends on the number of electrons contributing to the ferromagnetism. This property will have a marked influence on the permeability of materials which have been strained and deformed in any way, as well as on the domain formation.

The former is intimately connected with magnetostriction and we find that nickel is the only ferromagnetic showing negative magnetostriction, whilst no element shows positive magnetostriction at all fields and we must choose one of the permalloys as the best example of a typical case. It is known that if we apply tension to a rod of permalloy or compression to one of nickel, we assist the magnetization and increase the permeability. We can secure a thirty-fold increase in permeability in 68 permalloy (68% nickel, rest iron) in this way. These considerations apply to stresses below the elastic limit. Beyond this limit, stresses usually decrease the permeability of annealed materials, and the incidence of irreversible strain is often sharply reflected in changes of permeability. It is evident that not only can we cause drastic change in permeability by appropriate choice of direction of magnetization and accompanying strain, but by the combination of zero magnetostriction and crystal anisotropy we can obtain exceedingly high values of the permeability. It is significant that in the ternary system iron–silicon–aluminium the maximum permeability occurs at 10% silicon and 5·5% aluminium, where the anisotropy and the magnetostriction constants are both zero.

When a single crystal of a metal is elongated, slip occurs on a limited number of crystal planes that in general bear definite inclinations to the axis of tension. As elongation proceeds, the planes on which the slip occurs tend to turn so as to contain the direction of the tension. Thus a definite crystallographic axis may tend to lie in the direction of rolling of sheet material. This may be a direction of easy, or of difficult, magnetization, and so the magnetic properties along and perpendicular to the rolling direction can differ considerably, such that the permeabilities in the two directions can be in the ratio of as much as 20 : 1. Thus a 60–40% iron–nickel alloy suitably heat treated and annealed has a much greater permeability perpendicular to the direction of rolling than parallel to it by a ratio of about 15 : 1.[4] Rolled silicon–iron behaves similarly and has magnetic properties in accordance with those which would be derived from single crystal data. The data on undistorted single crystals are valuable because they provide an upper limit in permeability and a lower one in iron losses that manufacturers can regard as their highest possible achievement.

We must not omit to mention the applications of a magnetic field during heat treatment since they may make still easier the easy direction of magnetization and convert for example the three [100] easy directions in a body-centred cubic crystal to one only.

The magnetic powder technique as an aid to the study of domains has come into prominence with the introduction of electrolytic polishing. A colloidal suspension of iron oxide is applied to such a surface and these magnetic particles are attracted to the places where the intensity of magnetization is the greatest. These regions are the domain boundaries, i.e. the lines which separate regions magnetized in different directions. It is evident that the movements of these boundaries during the magnetization process can be followed by eye. It is a primary postulate of the Weiss theory of ferromagnetism that each domain is spontaneously magnetized and from our treatment of crystal anisotropy we can see that the easy direction of magnetization in the crystal will be the directions of magnetization in these individual domains. There are three such easy directions in iron, four in nickel and one only in what is virtually the uniaxial case of hexagonal cobalt. In the demagnetized state we have a random distribution of the magnetization along the easy directions, and as magnetization increases two processes take place, discontinuous changes from one easy direction to another more closely alined with the field, and also an actual movement of domain boundaries, such that those domains in which the magnetization has a large component along the field increase in size whilst those less favourably inclined diminish and finally disappear. What is known as the scratch technique can be employed to determine the direction of magnetization on particular domains. A light scratch produced with a fine fibre of glass is made on the surface under investigation and when this is parallel to the direction of magnetization no additional free poles are created and the powder pattern remains unchanged. On the other hand, when these are mutually perpendicular, the lines of magnetization in the substance are interrupted with the result that free poles are created and these are made visible by the colloid. The sense of the magnetization is determined from expansion or contraction of a domain during changes of an externally applied magnetic field. It is worthy of mention, however, that no quantitative correlation with the magnetization curve has yet been made. It would appear that those who employ magnetic powders for testing should be aware of the effects of domain boundaries. This argument is possibly fortified by the fact that Elmore[5] has used the same colloidal magnetic suspensions for both purposes.

The theory of eddy current penetration into a solid conductor, attenuation, angle of lag, and field amplitude, all involve the parameter $\sqrt{\mu f/\rho}$. The frequency f will be chosen with regard to the purpose of the experiment and determined largely by the thickness of the sample. For ferromagnetic materials, ρ varies little either from one ferromagnetic to another, nor does it change much with alloying, since its mean value of about 10^{-5} is the same as that for most ordinary materials. Thus the chief variable is the permeability μ and it has been shown above how this can vary with other physical factors, even though the composition remains unchanged. The most powerful feature of a.c. methods is that which is common to any a.c. bridge, i.e. control of both in-phase and out-of-phase components can be made simultaneously. Thus when these factors are demonstrated by a trace on a cathode-ray oscillograph for a sorting bridge, the identity of two dimensional traces provides strong evidence for passing the component, though this carries the implication that failure to secure this identity does not necessarily indicate inadequacy of the sample to fulfil its ultimate function.

There is also the geometry of the specimen under test to take into consideration. For example, electro-deposited films possess magnetic properties which vary with the thickness. The permeability of the three ferromagnetic elements is a maximum around 10^{-5} cm thickness, whilst the coercivity of nickel has its greatest value at the same thickness, this maximum is reached at one-tenth of that thickness for cobalt and iron. The orientation of the individual crystal grains may depend upon that of the layer already deposited. In general, the shape of the magnetization curve changes with thickness, and interpretation is uncertain. Whilst part of these changes are due to the self-demagnetizing factor, strain and change of crystal orientation with increasing deposition play their part.

There is one other important consideration implicit in the last paragraph which I feel I must mention because it is so frequently overlooked, as can easily be ascertained by a scrutiny of the literature. This is the failure to emphasize the fact that the applied field and the real field acting upon the specimen under test can be so vastly different. An instructive example can be taken from the variation of magnetic behaviour of the ordered alloy Fe_3Al with temperature. In low fields the magnetization falls very rapidly around 500° C and remains very low for some tens of degrees, but rises again to a sharp maximum at 570°, falling rapidly again at about 100° C. This was originally interpreted as a "double" Curie temperature, but magnetic measurements in high fields show little departure from the conventional intensity-temperature relationship, with a Curie temperature at about 600° C.[6] The explanation is found in the fact that ordered or completely disordered structures have high permeabilities, whilst the transition stages, with a mixture of ordered and disordered regions, have a low permeability. Considerable support for this view is found in two-phase magnetic systems. Thus it is seen that the degree of order can greatly influence the permeability.

As has been stated above, two-phase alloys may have low permeabilities, and high coercivities. This is largely due to the self-demagnetizing effects of small particles and can be illustrated by comparing the approach to saturation of spheres of the three ferromagnetic elements. The intensities of magnetization in an applied field of a thousand oersteds will show little if any difference. At three thousand oersteds

the nickel will show saturation effects, but there will be little to distinguish the intensities of the iron and cobalt, and it is only at about eight thousand oersteds that the intensities approach their saturation values. Thus any free poles, whether arising from the use of specimens on open circuit or the occurrence of cracks, reduce to a greater or less extent the applied field, and one must continually bear this in mind in magnetic testing.

OTHER POSSIBLE APPLICATIONS

The physical characteristics which have been dealt with above are the chief of those which I think are relevant in magnetic testing, but I would not omit to mention one or two other possibilities which may have some application. The first is in paramagnetism of the ferromagnetics above their Curie temperatures. These follow a law $\chi(T-\theta) = \text{constant}$, where θ is the Curie point and thereby a hyperbolic decrease of susceptibility with increasing temperature. Most other non-ferromagnetics show a temperature independence of the susceptibility. Thus face-centred cubic iron-austenite, is non-magnetic and the familiar γ loop shows itself in magnetic susceptibility measurements. At the phase change at 910° there is a discontinuous drop in the susceptibility to about one-sixth. There is then little variation until the sudden increase associated with the return to the body-centred cubic phase at about 1400° C.[7] For solid solutions of iron with other elements the change in limits of the γ loop can be followed by magnetic measurements. For example, iron–silicon has been investigated in this way.[8]

The possibilities of magnetic resonance will be dealt with in a separate contribution and so I can leave this without further reference. One other recent development, however, is that of neutron diffraction. The neutron diffraction pattern in general is a nuclear process, but there is an additional effect where the atoms have a magnetic moment, because the magnetic moment of the neutron interacts with the magnetic moment of the atom or ion, giving rise to a superposed pattern; the ordinary Bragg formula, containing the appropriate wavelength of the thermal neutrons employed, giving the magnetic lattice dimensions. In some cases, for example, nickel, the magnetic scattering amplitude is only 15% of the nuclear value, even in the most favourable (the forward) direction, and thus the intensity of the magnetic scattering is not detectable. In other cases, iron for example, the intensities are not so unfavourable and the diffraction pattern is such as would be expected from 2·2 units of magnetic moment—in agreement with established data. But one other important fact emerges. It has been implicitly assumed in our earlier consideration of iron, that the magnetic moments of all atoms were identical. An examination of the neutron diffraction pattern in detail precludes the possibility of there being two kinds of iron atom whose mean value is 2·2. One of the most powerful applications of neutron diffraction is to the study of cases where there are two or more interpenetrating lattices of ions of dissimilar magnetic moment. When these are equal and opposite we have the antiferromagnetic case, of which the best known example is manganese oxide. If on the other hand they are unequal but oppositely directed, we have the ferrimagnetics, including the ferrites, of which Fe_3O_4 is probably the most familiar example. Any such arrangement of unequal moments is precluded in the case of iron, thus making untenable the solution of Hume Rothery and others that there is in iron a combination of Fe^{++} ions and neutral Fe atoms. Similarly the suggestion of Zener that there are two types of Fe atom of five and one units oppositely directed is precluded. In both cases a superlattice line at (100) should be observed and this is entirely absent from the neutral diffraction pattern.[9] What impact these recent branches of physics will have upon the interests of the Non-Destructive Testing Group is difficult to forecast, but I submit that one should not lose sight of these rapidly developing subjects.

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Principles and applications of nuclear magnetic resonance

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The effect of the small magnetic moments of atomic nuclei can be detected by the principle of magnetic resonance. In a given magnetic field each nucleus with a spin and magnetic moment has associated with it a characteristic resonance frequency. Ordinarily, these resonances lie in the radio-frequency range and may be detected by radio techniques. Nuclear resonance may be used to detect the presence of particular isotopes and for the accurate measurement of magnetic field. The line widths of nuclear resonances in solids are primarily determined by magnetic interactions between nuclei and can provide useful information about internuclear distances. In liquids, molecular motion leads to extremely narrow resonances and fine structures of line may be resolved. These may be used for molecular structure determination and for the identification of chemical compounds. In metals, nuclear resonance frequencies are shifted by an effect due to the conduction electrons. This shift is related to the electronic structure of the metal. In addition to magnetic moments, many nuclei possess electric quadrupole moments which can interact with electric field gradients in a solid. Whilst in an ideal cubic lattice this interaction is zero, distortion produced by impurities or even mechanical treatment is often sufficient to broaden the magnetic resonance. This effect might be used to study defects in crystal structures.

INTRODUCTION

Nuclear magnetic resonance is a part of a new field of physics and chemistry which has been developed since the war. This subject, radio-frequency spectroscopy, utilizes the improved radio and radar techniques which are now available. In Fig. 1, the range of the radio-frequency part of the electromagnetic spectrum is shown with its relation to the more familiar infra-red and visible parts of the spectrum.

The approximate frequency ranges of the various types of radio-frequency spectra are shown. Paramagnetic resonance utilizes the interaction of the magnetic moment of the electron with a magnetic field and nuclear quadrupole spectroscopy depends on the interactions of nuclear electric quadrupoles in the absence of a magnetic field. In addition, in the microwave region, we have ordinary molecular spectra concerned

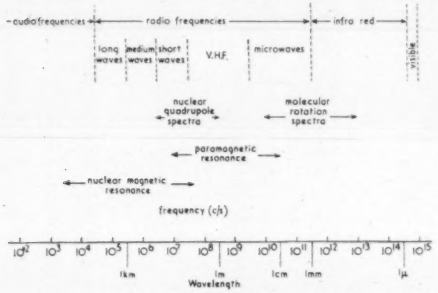

Fig. 1. The scope of radio-frequency spectroscopy

with the rotational and vibrational levels of molecules. In nuclear magnetic resonance, the frequencies involved usually lie in the range 1–30 Mc/s though experiments can be done using frequencies as low as 2 kc/s or less.

NUCLEAR SPINS AND MOMENTS

The basis of the technique of nuclear magnetic resonance is the fact that many nuclei possess both magnetic moments and angular momentum or "spin." Some examples are given in the table. By quantum mechanics, we know that angular momentum must be a multiple of $h/2\pi$, where h is Planck's constant, i.e. $Ih/2\pi$ where I has integral or half-integral values. I is called the "spin" of the nucleus.

The unit usually used for magnetic moments of nuclei is the nuclear magneton defined as follows:

$$\mu_{nucl} = eh/4\pi Mc = 5{\cdot}049 \times 10^{-24} \text{ e.m.u.} \qquad (1)$$

where e is the electronic charge in e.s.u., c the velocity of light and M the mass of a hydrogen nucleus or proton. This definition is analogous to that of the Bohr magneton used for electronic moments. The mass M of a proton has been substituted for the very much smaller mass m of an electron. The nuclear magneton is thus a very much smaller unit than the Bohr magneton, the ratio of the two units being that of the masses of the electron and proton. Since the electron has a magnetic moment of almost exactly one Bohr magneton, it might be supposed that the proton would have by analogy a moment of one nuclear magneton. This expectation is, however, only correct as to order of magnitude; in fact, as will be seen from the table, the proton has a moment of nearly 3 nuclear magnetons. The magnetic moments of the other nuclei obey no obvious quantitative rules although some generalizations can be made. There are about 130 nuclei known to have spins and magnetic moments. These nuclei may in principle be used in magnetic resonance experiments. The hydrogen nucleus or proton is particularly useful since it has a favourable spin and magnetic moment and is of great interest to chemists and crystallographers.

NUCLEAR PARAMAGNETISM

Compared with electronic moments, nuclear moments are very small (of the order of a thousand times less), so that any magnetic effects associated with nuclei are likely to be several orders of magnitude smaller than the corresponding electronic effects. The influence of nuclear moments on the ordinary magnetic properties of matter is usually entirely negligible. However, nuclei do give rise to a paramagnetic effect which may be calculated.

In the simple theory of paramagnetism, we consider an assembly of magnetic moments which are free to orientate themselves when a magnetic field is applied. In the absence of a field, the magnetic moments are oriented at random. On applying a field H, they tend to aline themselves along the direction of H, giving the specimen a resultant magnetic moment. The susceptibility is given by

$$\chi = \frac{N\mu^2}{3kT}\left(\frac{I+1}{I}\right) \qquad (2)$$

Nuclear spins and moments

Nucleus	*Spin units of* $h/2\pi$	*Magnetic moment Nuclear magnetons*
^{1}H	$\frac{1}{2}$	2·7927
^{2}H	1	0·8574
^{19}F	$\frac{1}{2}$	2·6273
^{27}Al	5/2	3·6385
^{35}Cl	3/2	0·8209
^{37}Cl	3/2	0·6833
^{63}Cu	3/2	2·2206
^{65}Cu	3/2	2·3790
Electron	$\frac{1}{2}$	−1836

where N is the number of moments per unit volume, k is Boltzman's constant and T the absolute temperature. The magnetic moment of each particle μ enters as the square so that nuclear paramagnetism is generally about a million times weaker than electronic paramagnetism. Whereas at ordinary temperatures, electronic susceptibilities are of the order of 10^{-3}, nuclear susceptibilities are only of the order of 10^{-9}. As ordinary diamagnetism gives susceptibilities of the order of 10^{-6}, it is not feasible to detect directly the presence of nuclear magnetism, except perhaps at very low temperatures. For example, in water at room temperature, there is a diamagnetic susceptibility of $7{\cdot}3 \times 10^{-7}$ whereas the paramagnetic susceptibility due to the protons is only $3{\cdot}2 \times 10^{-10}$; thus, were it not for the principle of magnetic resonance, we should not be able to detect the presence of nuclear magnetism in ordinary matter. Even with nuclear resonance, we are dependent on a net orientation of the nuclei in the field. If there is no net magnetic moment in the direction of the field the resultant resonance effect will be zero.

THE PRINCIPLES OF MAGNETIC RESONANCE

For simplicity consider a particle (such as the proton or electron) with a spin $\frac{1}{2}$ in a magnetic field H. From quantum mechanics there are two possible orientations of the spin; parallel and antiparallel to the magnetic field. The energies of these states are $-\mu H$ and $+\mu H$ respectively. We may induce transitions between these two states by the application of an electromagnetic field of frequency ν given by the usual Bohr relation:

$$h\nu = 2\mu H \qquad (3)$$

It is more usual to express this relation in terms of a quantity γ the gyromagnetic ratio which is defined as the ratio of the magnetic to the mechanical moment of the particle.

$$\gamma = \frac{\mu}{(Ih/2\pi)} \tag{4}$$

Remembering that $I = \frac{1}{2}$ in the case we have chosen, equation (3) becomes

$$2\pi\nu = \gamma H \tag{5}$$

This relation is true for any spin and is the fundamental equation of magnetic resonance.

γ is a constant for each nucleus so that for a given nucleus in a given magnetic field, there exists a characteristic frequency at which transitions take place and energy can be absorbed. If we consider the problem by classical mechanics, this same frequency would appear as a natural precession frequency of the system. This frequency is called the resonance frequency of the system. For most nuclei in fields which are ordinarily produced in the laboratory, these frequencies lie in the range 1–30 Mc/s, i.e. in the radio short wave band. For example in a field of 5000 G, the resonance frequency for protons is about 21 Mc/s and for ^{107}Ag nuclei (which have a very small magnetic moment), 862 kc/s.

It may be shown that the type of electromagnetic field which will produce these transitions at resonance is a magnetic field perpendicular to the main field and rotating at the resonance frequency. The arrangement for nuclear magnetic resonance therefore consists of a large static field H and a small radio-frequency field applied in a perpendicular direction. In practice we do not usually use a rotating field but simply an oscillating field which may be decomposed into two rotating components, one of which is effective.

THE DETECTION OF NUCLEAR MAGNETIC RESONANCE

Having induced transitions between energy levels in a magnetic field, we now come to the problem of how to detect them. One straightforward method utilizes the techniques of molecular beams. The spins are actually sorted out into those parallel and antiparallel to the field. This method is not, however, very convenient or universally applicable and it must be considered a real advance when resonances were picked up from ordinary matter. Apart from the advantage of the simplicity of the apparatus, this method provides the possibility of studying the interaction of nuclei with internal electric and magnetic fields in a substance. This aspect has proved to be most productive. Nuclear magnetic resonance in ordinary matter was first found by Bloch, Hansen and Packard[1] at the University of California and independently by Purcell, Torrey and Pound[2] at Harvard in 1946. Bloch and Purcell jointly received the Nobel prize in Physics for 1952 for this work.

Both workers looked for protons, Bloch in water and Purcell in paraffin wax. Bloch called his method nuclear induction and Purcell nuclear resonance absorption. The principles of the methods are fundamentally the same. They depend on the fact that when transitions are taking place there exists a macroscopic component of magnetic moment rotating at the resonance frequency. This can induce a voltage in a suitably placed receiving coil. The existence of this rotating moment may be readily understood as it provides a mechanism by which energy can be absorbed from the radio-frequency field into the specimen. In Purcell's system one coil only is used. This serves both to provide the radio-frequency exciting field and also to receive the signal from the resonance. Bloch's system uses two coils whose axes are at right-angles. One coil provides the radio-frequency field and the other is for receiving the signal. The advantage of this system is that the direct coupling between the coils is small and thus the stray pick-up against which the signal must be detected is small. This makes the process of amplification easier. The main disadvantage is, of course, that the coil system surrounding the specimen is more complicated than with the single coil method.

An apparatus for observing nuclear magnetic resonance is illustrated diagrammatically in Fig. 2. The main magnetic

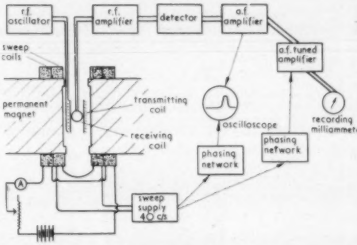

Fig. 2. Diagram of an apparatus for observing nuclear magnetic resonance. The sample is placed inside the receiving coil

field may conveniently be provided by a permanent magnet. Subsidiary coils are employed to produce the small variations in field which are required. Both a.c. and d.c. variations can be supplied. A convenient size for the specimen is about 1 cm^3. The signal from the receiving coil may, after suitable amplification and detection, be displayed on an oscilloscope. In the most usual method of presentation, the frequency of the oscillator is kept constant. Resonance will then occur for a particular value of the magnetic field given by equation (5). If we plot signal strength against field a peak will be obtained at the value of the field which corresponds to resonance with the oscillator frequency used. A specific example is shown in Fig. 3 where the signal from a sample containing protons is plotted against magnetic field. If the frequency employed is 20 Mc/s, a peak is found at a magnetic field of 4697 G. A simple method of display is to put the

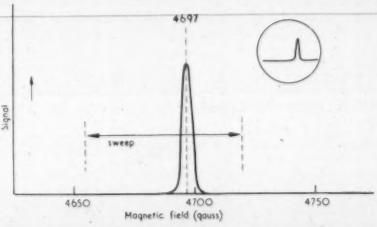

Fig. 3. A plot of a magnetic resonance signal against magnetic field for protons at a frequency of 20 Mc/s. *Inset*—Oscilloscope pattern when resonance is displayed using the sweep field shown

signal on to the Y-plates of an oscilloscope and to sweep the field to and fro over a range containing the resonance value by means of the coils on the magnet. If a voltage proportional to this sweep field is applied to the X-plates of the oscilloscope, a plot of signal against field is obtained on the oscilloscope screen which will show the presence of a resonance.

When weak resonances are being observed or when accurate plots of nuclear resonance line shapes are being made, a more sensitive method of plotting resonances can be used. A small a.c. sweep is used which in the resonance region gives rise to an a.c. signal proportional to the derivative of the resonance curve. This may then be amplified and sorted out from noise and interference by an extremely selective audio-frequency tuned amplifier. In this way, satisfactory resonance curves may be obtained from signals of a strength of only 1/1000 of that which may be satisfactorily displayed on an oscilloscope.

DIRECT APPLICATIONS OF NUCLEAR MAGNETIC RESONANCE

The principle of nuclear resonance may be utilized directly in a number of ways. Firstly, if we make a measurement of the frequency and magnetic field required for a resonance, the gyromagnetic ratio of a nucleus may be determined. If the nuclear spin is known, the magnetic moment may be determined with considerable accuracy. This is useful information for nuclear physicists. The method permits the sign of the nuclear moment to be determined.

Secondly, the observation of a resonance at a position characteristic of a particular nucleus shows the presence of those nuclei in the sample, i.e. the method may be used for the measurement of the isotopic constitution of a sample. The method may thus be used to detect elements which have isotopes with magnetic moments.

Thirdly, using a given nucleus such as the proton, magnetic fields may be determined. From equation (5), it will be seen that there is a strict relation between magnetic field and frequency at resonance. The measurement of magnetic field thus resolves itself into the measurement of the frequency at which resonance occurs. Frequency can be measured easily to a very high accuracy (1 part in 10^6 without much difficulty). The accuracy with which the resonance position can be found depends, of course, on the width of the resonance. Natural line widths are not a limiting factor as widths as small as 1 part in 10^7 can be obtained with liquid samples. The accuracy will in practice be limited by the homogeneity of the field. A reasonable degree of homogeneity is required for the method to work but for fields for which the method is suitable, the method is very quick, accurate and reliable. Though the main application is for fields of thousands of gauss, much smaller fields can be measured if a sufficiently large volume of uniform field is available. For example, the earth's field (0·4 G) can be measured. Here the resonance frequency of protons is only about 2000 c/s.

LINE BROADENING

In the foregoing discussion, the influence of the environment of the nucleus has not been considered. The resonance has been assumed to be unaffected by the exact chemical compound or physical state of the substance in which the nuclei under observation find themselves. It is generally true that the environment has a very small effect on the position of a nuclear resonance. Such effects called "shifts" of the resonance though small are frequently measurable and can provide useful information. The environment also affects the width and structure of a resonance line. A third way in which it is important is in the mechanism of spin-lattice relaxation, i.e. how energy is transferred from the nuclear spins to the lattice.

Let us first consider the effect on line widths as line broadening is the most obvious and important effect of the surrounding of the nuclei. Line broadening means that the resonance is to some extent spread out over a range of frequencies instead of occurring at precisely one frequency in a given field. If we keep the frequency constant, then the resonance becomes spread out over a range of magnetic fields. Thus line width may be expressed either in field units, gauss, or frequency units, kc/s.

Experimental conditions can affect the apparent line width of a resonance. This is because magnetic fields produced in the laboratory are not perfectly homogeneous. Thus different parts of the specimen are in different magnetic fields and so come into resonance at different frequencies. In nuclear magnetic resonance work, it is thus important to ensure that the magnetic field is extremely homogeneous. Uniformities of 1 part in 10^4 over the specimen are usually sufficient though for some work 1 part in 10^7 is required.

Apart from field inhomogeneities, the most important source of line-broadening in a diamagnetic material comes from magnetic interactions between nuclei. Let us consider 2 spins μ_1 and μ_2 separated by a distance r (Fig. 4). Let θ

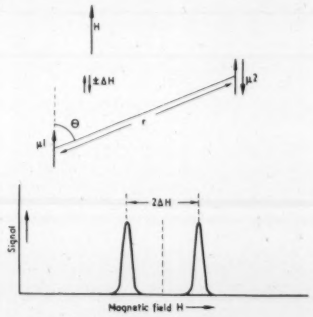

Fig. 4. The magnetic interaction between two spins produces a magnetic resonance doublet

be the angle the vector joining μ_1 and μ_2 makes with the applied field H. The magnetic field at μ_1 is dependent on whether the spin μ_2 is parallel or antiparallel to the field. There are two possibilities $H - \Delta H$ and $H + \Delta H$ where ΔH is the local field produced by μ_2

$$\Delta H = \mu_2(3\cos^2\theta - 1)/r^3 \qquad (6)$$

The resonance is thus split into a doublet of separation $2\Delta H$. It will be noted that the separation depends on the orientation of the vector joining the nuclei.

The best example of a resonance from a system of 2 spins is in gypsum, $CaSO_4 . 2H_2O$.[3] In this substance, protons are the only nuclei with magnetic moments and they occur in pairs in water molecules. From the separation of the proton resonance doublet, the distance between hydrogen atoms may be found. This is an example of another applica-

tion of nuclear resonance, the determination of internuclear distances in crystals.

When there are three spins interacting with each other, the spectrum becomes much more complicated and when a large number of spins are involved the structure of the resonance is so complex that it is no longer resolved. Only a single broad line is observed. The width of the line gives a measure of the mean distance between nuclei in the material.[4] As an example of a resonance which is broadened almost entirely by this dipole-dipole interaction between many spins we may consider calcium fluoride CaF_2.[5] Here the ^{19}F resonance has a roughly Gaussian shape and a line width of about 5 G.

THE EFFECT OF MOLECULAR MOTION

Whilst line widths in solids are generally well explained by the magnetic dipolar interaction which has been considered, line widths in liquids are very much smaller than would be expected on this basis. In water the average spacing of the protons is 2·5 Å and we might thus expect a line width of 5 G. Actually, the width is found to be less than a milligauss. There must evidently be some mechanism of line narrowing. The explanation is found in the motion of the molecules. Bloembergen, Purcell and Pound[6] have worked out the theory of this in detail. To explain this effect, let us return to the consideration of the magnetic interaction between two nuclei. If the average value of ΔH given by equation (6) is taken over all possible orientations of the vector joining the two nuclei, the resultant is zero. In a liquid, molecules move around one another sufficiently rapidly for this averaging procedure to be valid. To achieve this effect, it is necessary that the local magnetic fields average out to zero in a time short compared with the life-time of the nuclear spin states. This time, in fact, depends on the spin-spin interaction and is usually of the order of 10^{-4} to 10^{-5} s. The rate of molecular motion in a liquid can be slowed down by cooling. In glycerine, a liquid which can be supercooled easily, the transition from a line width characteristic of a liquid to that of a solid can be followed as the temperature is reduced. A plot of line width against temperature shows a transition.

The marked difference between the line widths of nuclear magnetic resonance in the solid and liquid states may be applied to detect liquid impurities such as moisture, in a solid material. The sharp resonance of the liquid stands out clearly against the broad background of the resonance from the solid. The effect of molecular motion is also often important in solids. A partial narrowing of a magnetic resonance line may often be attributed to the rotation of a group of atoms. The classic example of this type is ammonium chloride,[7, 8] NH_4Cl, in which at ordinary temperatures the magnetic interaction between protons in the same ammonium ion is averaged to zero by the hindered rotation of the NH_4 group. A plot of the line width of the proton resonance against temperature shows a transition (Fig. 5). Most other ammonium salts and many other substances, especially solid organic compounds, show similar transitions. The temperature at which the transition takes place is an indication of the potential barrier to the type of motion involved.

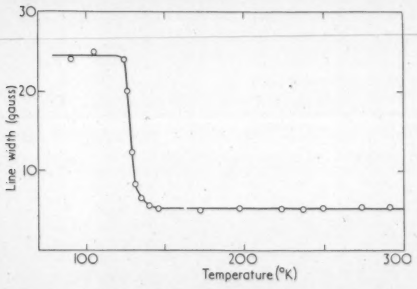

Fig. 5. A plot of proton magnetic resonance line width against temperature for ammonium chloride

Perhaps even more remarkable is the narrowing due to the interchange of atoms on a solid lattice. This mechanism can produce a line as narrow as that in a liquid. In metallic sodium[9] (Fig. 6) there is a transition in the line width of

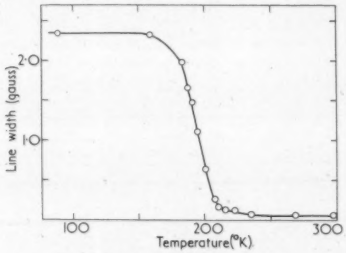

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Fig. 6. A plot of magnetic resonance line width against temperature for ^{23}Na nuclei in sodium metal

the ^{23}Na resonance at about 180° K. The line width of 2·2 G arising from the normal magnetic dipole-dipole interaction is reduced practically to zero above the transition. The narrowing is attributed to the interchange of Na atoms in the lattice. This effect is, of course, also responsible for self-diffusion and the rate of self-diffusion may be estimated in this way.

HIGH RESOLUTION NUCLEAR MAGNETIC RESONANCE

It was mentioned earlier that shifts in the position of nuclear magnetic resonances, though small, are frequently important. This is particularly true of liquids. As we have seen, nuclear magnetic resonance lines in liquids can be extraordinarily narrow as a result of molecular motion. Consequently it is possible to detect shifts as small as 1 part in 10^7. The natural width of lines in liquids is usually governed by nuclear spin-lattice relaxation times. These may be of the order of a few seconds and it follows that the natural line width may be of the order of $\frac{1}{2}$ c/s or less. For protons, this is equivalent to only 0·2 mG. Thus to observe the ultimate width of a proton resonance in a liquid in a field of several thousand gauss, a field homogeneity of 1 part in 10^8 may be required. This requirement places considerable strain on the design of a magnet. However, it is now possible to obtain magnets whose field is homogeneous to 1 part in 10^7 over a small specimen. A very large and carefully constructed magnet has to be used to get the required homogeneity over a specimen a few millimetres across.

The use of these extremely uniform magnetic fields has opened up a new field of nuclear magnetic resonance, high resolution N.M.R. The application of this technique has yielded a wealth of fine detail about the structure of magnetic resonances in liquids. The structure of the resonance seems to get more complicated as the limit of resolution is pushed back. The proton resonance from ethyl alcohol under high resolution[10] is shown in Fig. 7. In Fig. 7(*a*) the resolution is sufficiently good to show the separation of the resonances due to the protons in the CH_3, CH_2 and OH groups. The effect is due to the different shifts produced by the electrons

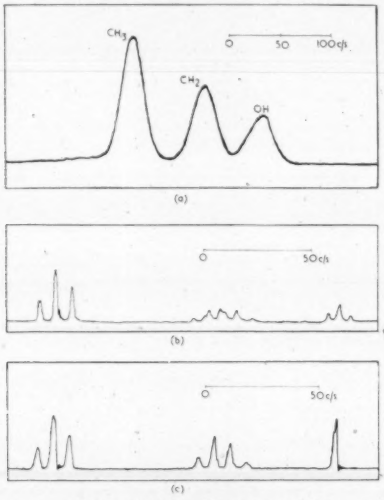

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Fig. 7. Proton magnetic resonance from ethyl alcohol

(*a*) Moderate resolution showing the separation of the resonances from chemically non-equivalent protons.
(*b*) High resolution spectrum from pure material.
(*c*) High resolution spectrum of impure ethyl alcohol showing the effect of chemical exchange.

of the molecule at these three chemically non-equivalent positions. The higher resolution of Fig. 7(*b*) shows the triplet structure of the resonance from the CH_3 group and the quadruplet structure of that from the CH_2 group. Even higher resolution than that shown produces even more detail. The effect of a small trace of impurity on the proton resonance from ethyl alcohol is shown in Fig. 7(*c*). This differs from Fig. 7(*b*) in that the multiplet structure of the resonance from the OH group has been lost. This is a result of a sufficiently rapid chemical exchange of protons in the OH groups of different molecules.

Each chemical compound produces a characteristic nuclear magnetic resonance spectrum under high resolution. The method could thus be used for the identification of a chemical compound in a mixture or for quantitative analysis. In addition, the structure of the resonance spectrum is closely related to the structure of the molecule and thus may be useful for elucidating unknown chemical structures. The structure of diborane[11] has been determined in this way. Thus high resolution nuclear magnetic resonance promises to be a very important tool for the chemist.

NUCLEAR RESONANCE IN METALS

There is an important shift of magnetic resonance frequencies in metals. In contrast to the minute shifts involved in high resolution work, the shifts in metals are quite appreciable and can be measured even against the large dipole-dipole broadening of a solid. Examples of the magnitude of this shift are aluminium, 0·16%; copper, 0·23%; thallium, 1·5%. This effect, called the Knight shift after its discoverer, is characteristic of metals and is due to the conduction electrons which are capable of being polarized by the magnetic field and so producing a subsidiary magnetic field at the nuclei. The conduction electrons are comparatively strongly coupled to the nuclei because they have *s*-type wave functions which have maxima at the centres of the atoms. It is thus seen that the shift is related to the electronic structure of the metal. The shift may be quite different in different modifications of the same metal. For example, in white tin the shift is 0·75% but 0·0% for the grey modification.

NUCLEAR QUADRUPOLE EFFECTS

Another class of application of nuclear magnetic resonance arises from electric quadrupole moments of nuclei. These moments arise from a lack of symmetry in the charge distribution in nuclei. One could imagine, for example, that the positive charge in the nuclear structure has a higher density near the ends of the nuclear spin axis instead of being uniformly distributed over the whole volume. This type of asymmetry is characterized by a quadrupole moment, a number specifying the deviation from spherical symmetry.

While the energy of interaction of the quadrupole with a homogeneous electric field is zero, there is an energy of interaction with an inhomogeneous field, i.e. an electric field gradient. To see how a quadrupole interaction affects the nuclear magnetic resonance, let us consider the simplest case, a nucleus with a spin of 1. (Nuclei with spin $\frac{1}{2}$ do not exhibit quadrupole effects.) A nucleus of spin 1 in a magnetic field has three possible energy levels corresponding to magnetic quantum numbers $m = +1, 0$ and -1. These are illustrated in Fig. 8. The magnetic resonance results from transitions

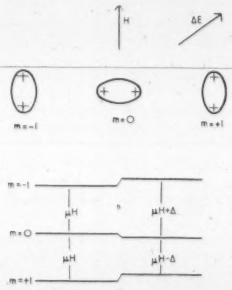
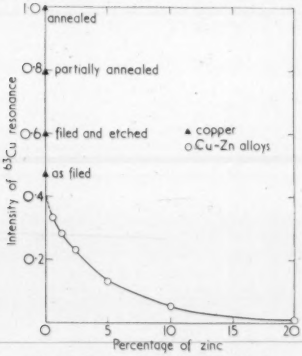


Fig. 8. The perturbation of magnetic resonance levels by electric quadrupole interactions for a nucleus of spin 1

between adjacent energy levels. In the absence of the perturbing electric field, the energy differences corresponding to the transitions $m = -1$ to $m = 0$ and $m = 0$ to $m = +1$ are the same, so that a single resonance line is observed. The effect of an electric field gradient ΔE is to change the energies of the levels. The levels $m = +1$ are moved by the same amount as there is no difference electrically between nuclei pointing in exactly opposite directions. The middle state, $m = 0$ will be shifted by a different amount, and in the opposite sense. Transitions between adjacent levels now lead to a doublet. For spins greater than 1, multiplets will be observed.

In single crystals, one may resolve the multiplet structure of a nuclear resonance due to quadrupole splitting. From the splitting, the electric field gradient in the crystal may be determined. In a powdered sample, however, no well-defined structure of the resonance will be observed as the orientation of H and ΔE will not be constant throughout the specimen. A general broadening of the resonance only will be observed. If the line broadening is excessive, there results a considerable diminution in signal intensity or even the effective obliteration of the resonance signal.

When the surroundings of the nucleus have cubic symmetry as often happens in a perfect cubic crystal, quadrupole interactions vanish. This is because symmetry considerations imply that the electric field gradient is zero at a centre of cubic symmetry. Thus in pure copper the surroundings of a copper nucleus are cubic and hence no quadrupole broadening of the resonance is observed. If, however, physical or



[Reproduced from *Acta Metallurgica*]

Fig. 9. The intensity of the ^{63}Cu magnetic resonance in pure copper and in copper–zinc alloys

chemical impurities are added by mechanical work or alloying, the surroundings of those copper nuclei close to an impurity deviate significantly from cubic symmetry and quadrupole broadening is obtained which leads to a diminution of signal strength. Fig. 9 shows how the signal strength from the ^{63}Cu resonance decreases when zinc is added to pure copper.[12] The reference for unit intensity is pure well-annealed copper. For ^{63}Cu whose spin is 3/2 the quadrupole broadening occurs in two stages. This arises from the fact that the central line of the quadrupole triplet structure is unchanged to a first approximation. Thus the central line remains until the quadrupole interaction is much greater than that required to remove the satellite lines. For a spin of 3/2, 0·4 of the resonance intensity lies in the central line and thus it appears from Fig. 9 that, in copper, cold work is sufficient to remove the satellite lines of the ^{63}Cu resonance. Adding zinc increases the quadrupole effect so much that the central line is affected. When more than 20% zinc has been added, the resonance is no longer observable.

SUMMARY OF APPLICATIONS OF NUCLEAR MAGNETIC RESONANCE

It has been seen how nuclear magnetic resonance can be of value in many branches of physics and chemistry. As the method is essentially non-destructive in character, it is extremely probable that one or more of the possibilities outlined will find application in non-destructive testing. To summarize, here is a list of some of the applications or possible applications which have been suggested:

(1) Measurement of nuclear magnetic moments.
(2) Isotopic analysis.
(3) Measurement of magnetic field and field homogeneity.
(4) Determination of internuclear distances.
(5) Determination of liquid content, e.g. moisture.
(6) Investigation of molecular rotation.
(7) Self-diffusion measurements.
(8) Chemical analysis (high resolution).
(9) Molecular structure determination (high resolution).
(10) Chemical exchange (high resolution).
(11) Electronic structure of metals.
(12) Measurement of electric field gradients in crystals.
(13) Defects or impurities in solids.

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Optical fluorescence in non-destructive testing

By W. A. Runciman, B.Sc., A.Inst.P., Atomic Energy Research Establishment, Harwell, Berks.

Fluorescence techniques have a wide range of applicability. In non-destructive testing they are used for the detection of X-rays, and also in the examination of metals. Magnetic materials can be tested by the fluorescent magnetic particle method, and the surface of any metal can be inspected for cracks using the fluorescent penetrant method. The main properties of the luminescent centre are outlined with a view to obtaining a deeper understanding of the processes involved, and to applying them to further types of problem. Examples of fluorescent substances include pure and impurity-activated solids, both organic and inorganic. Metals are non-fluorescent, but materials which can be directly studied by fluorescence include some glasses, ceramics and textiles.

INTRODUCTION

Fluorescence must be a phenomenon known to all in the field of non-destructive testing as it has long been used in intensifying and fluoroscopic screens for the detection of X-rays. Intensifying screens are usually made with calcium tungstate, and for fluoroscopic screens the most commonly used material is silver-activated zinc cadmium sulphide.[1] The fluorescent screen may be directly observed, or as in the case of mass radiography it may be photographed to provide a permanent record.

Another familiar application of fluorescence concerns the examination of metals. Magnetic materials can be tested for irregularities on or near the surface by the fluorescent magnetic particle method, and the surfaces of any metal, and of some non-metals, can be inspected for cracks by the fluorescent penetrant method.[2] In this method the specimen is dipped into a fluorescent penetrant, the surface is cleaned and dried, and then dusted with a developing powder which draws the penetrant out of any cracks. The cracks are then easily visible under an ultra-violet "black" lamp. The method has been made more sensitive recently by the use of the post-emulsification technique,[3] in which the emulsifier is applied after the penetration of the organic fluorescent dye. Owing to the tendency of emulsifiers to reduce the depth of penetration, this new technique can be applied to find finer cracks.

The physical processes involved in luminescence will now be outlined to provide a basis for the discussion of new possibilities.

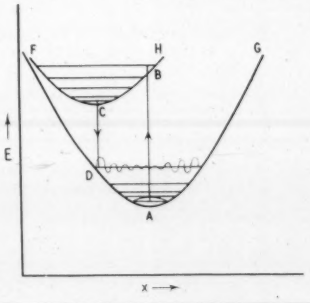
THE NATURE OF LUMINESCENCE

Luminescence occurs when a substance emits light with a wavelength characteristic of the substance. Such a luminescent material is often called a phosphor—even when it is not phosphorescent! The phosphor first has to absorb incident energy, which may consist of atomic particles or X-rays (in scintillation counters), electrons (in cathode-ray tubes or television screens), X-rays (in fluoroscopy), or ultra-violet radiation (in fluorescent lighting). In the case of ultra-violet or visible radiation, the absorbed light has usually a greater quantum energy than the emitted light, but when there is equality in energy, and hence in wavelength, the emitted light is called resonance radiation.

Fluorescence describes the process of light emission in cases where there is a simple de-excitation of the luminescent centres; phosphorescence relates to the case where the light is emitted only after the energy is released from trapping states in the solid. A phosphorescent decay may range from a fraction of a second to several hours, whereas the half-lives of the simple exponential decay in fluorescence are usually in the range 10^{-9} to 10^{-3} s.

Fluorescent light is emitted from centres in the solid, and these centres may be either single ions or groups of ions. Some pure substances, e.g. anthracene or uranyl nitrate, are luminescent, but very often the fluorescence is characteristic of a small amount of impurity added to the base material, e.g. thallium activated potassium iodide [KI(Tl)]. In more complex cases more than one impurity ion may have to be present in the lattice, either because the emitting ion does not absorb the incident radiation or because charge compensation is necessary for the ion to be incorporated in the lattice in the proper valency state.[4]

Let us consider in more detail a simple fluorescent system in which an impurity ion replaces an ion of the base lattice and acts as a luminescent centre. Thallium activated potassium chloride [KCl(Tl)] is a system of this type which has been extensively studied both experimentally and theoretically.[5] The configuration co-ordinate diagram shown in the figure is a convenient aid to the understanding of this system.



Configuration co-ordinate diagram

In this diagram one spatial co-ordinate x, perhaps the distance of nearest neighbours from the activator ion, is picked out as representative of all the atomic co-ordinates necessary to specify the system. The luminescent centre in its ground state is represented by the potential energy curve FG, which is nearly parabolic. The ordinate E is the energy of the luminescent centre, and at low temperatures the energy level will be near the bottom of the parabola. It can never quite be at the lowest point because of the zero point energy. The approximate shape of the lowest wave function is shown, it being a maximum above the minimum of the parabola. In contrast the wave function of one of the vibrationally excited states is oscillatory with maximum amplitude near the parabola. When ultra-violet light is absorbed the transition

AB takes place to a point near the upper parabola *FH*, which represents the electronically excited state of the luminescent centre. The configuration co-ordinate x cannot alter during the transition if the Franck–Condon principle is to hold. (The Franck–Condon principle asserts that during an electronic transition the positions and momenta of atomic nuclei are substantially unchanged.) The luminescent centre then relaxes to a point near the minimum of the upper parabola before the emission of a visible quantum of fluorescent radiation in the transition *CD*. The centre again dissipates energy as heat in reverting from *D* to the initial position *A*.

Unfortunately this picture is oversimplified for any real system, because of the reduction in symmetry of the excited state which occurs as a result of the Jahn–Teller effect, and because of the changes in polarization of the ions in the vicinity of the activator ion. (The Jahn–Teller effect states that a crystal lattice will distort if this will remove the degeneracy of the electronic state of an ion in the crystal.) Normally the vibrational fine structure of the energy levels within either the ground or excited state of the luminescent centre is so complex that the absorption and emission spectra consist of broad bands. However, in some instances the vibrational fine structure is resolved, e.g. in CaO(Bi); and in other phosphors, especially those activated by rare-earth or transuranic ions, the electric crystalline field produces an easily detectable Stark splitting of the levels. In brief, the phenomenon of fluorescence is one of the electronic excitation of an atom or group of atoms with perturbations due to the surrounding ions in the solid.

MORE COMPLEX SYSTEMS

Many phosphor systems—if not all—have a more complicated behaviour than would be expected on the above model, and a brief résumé follows of some of the phenomena which occur.

Sensitized luminescence. In many phosphor systems the energy is absorbed by one set of impurity ions and is then transferred to the other set of impurity ions. Thus although the luminescence is characteristic in its emission band of one impurity, the system is not fluorescent if only that impurity is added to the base material. There is still uncertainty about the way the two sets of ions are distributed in the lattice and about the nature of the energy transfer process.

Photoconductivity. Sulphides are examples of phosphors which are photoconducting on the absorption of ultra-violet radiation capable of producing fluorescence. This means that an electron in the excited state is not localized as in the figure, and it is necessary to consider the energy band scheme of the whole solid.

Phosphorescence. An electron in the conduction band may get trapped at a defect, and as the traps gradually get emptied by thermal agitation the luminescent centres can return to the ground state accompanied by light emission. This process may go on for hours after the excitation of the phosphor. The analysis of the process is complicated by possible retrapping of the electron, and by the existence of many trapping levels.[6]

Thermoluminescence. The deepest traps in a phosphor can only be emptied at an appreciable rate by heating the phosphor to several hundred degrees Centigrade. A glow curve is obtained by plotting the light output as a function of temperature in an experiment where the rate of temperature increase is kept constant. It is unfortunately not possible to get a complete picture of the trapping states by this type of experiment due to the occurrence of radiationless transitions to the ground state.

Infra-red stimulability. Yet another way of releasing stored energy in phosphors is by infra-red irradiation. As in the case of sensitized luminescence two activators are present. Calcium or strontium sulphide activated by europium and samarium show the effect, the stimulation spectrum being characteristic of the samarium and the emission being characteristic of the europium. In other instances infra-red irradiation causes a quenching of the phosphorescence.

EXCITATION OF LUMINESCENCE

When a phosphor is excited by highly energetic radiation, e.g. X-rays, the incident radiation has to be subdivided by secondary electron formation until the luminescent centre can absorb the few electron volts necessary for excitation. The efficiency of this process can be expected to be low and may be of the order of one-tenth. On the other hand with ultra-violet excitation the process may be of the type illustrated in the figure, and the quantum efficiency may be very close to unity. There is, of course, some energy loss due to the degradation in energy from ultra-violet to visible radiation.

The commonest sources of ultra-violet radiation are the low-pressure mercury vapour lamp for 2537 Å, and the high-pressure mercury vapour lamp for 3650 Å. Both these lamps can have undesirable visible radiation removed by solid or liquid filters. In the case of the high-pressure lamp filter material can be incorporated into the outer glass bulb. This "black" lamp emits a considerable amount of continuum in the near-ultra violet in addition to the strong triplet at 3650 Å; whereas the low pressure lamp concentrates most of its light in the resonance line at 2537 Å.

For geological survey work it has been found possible to make battery-operated models of these lamps, and the lamps have been incorporated into many types of fluorimeter developed for specific applications. For instance, fluorimeters designed for the microfluorimetric determination of uranium measure quantities down to 10^{-10} g using the sodium fluoride fusion method, and even smaller quantities of uranium may be detected.

APPLICATIONS OF FLUORESCENCE

There have been many applications of fluorescence techniques to analysis, and one book lists 3500 references,[7] some of which may have a bearing on non-destructive testing. It is noteworthy that fluorescence methods are essentially non-destructive, although there may be a few cases of photo-decomposition or fading if ultra-violet irradiation is prolonged. Fluorescent materials include organic and inorganic compounds, minerals, gemstones, glass, paper, textiles, ceramics, food and drugs.

Even if the material under investigation is not fluorescent it may still be possible to use fluorescence techniques by adding a fluorescent tracer in a similar way to the use of radioactive tracers. This might be useful in a study of mixing techniques. Metals may be tested by the use of fluorescent penetrants for the detection of surface flaws, and the porosity of materials can be tested in a similar way. Luminescent substances have efficiencies which are dependent on temperature, and this or thermoluminescent effects may provide a basis for checking the temperature over large surface areas. The efficiency of luminescence may also be affected by the amount of high-energy irradiation received. Because of this fluorescent glasses can be used in dosimeters, and there are other possibilities in the study of radiation damage in solids.

Many substances fluoresce most strongly at low temperatures, and there is scope for the microscopic investigation of fluorescent minerals at liquid air temperature. This would be especially valuable in spotting traces of secondary uranium minerals. In general, it is advisable to test for fluorescence with more than one type of excitation and, if possible, at liquid air temperature as well as at room temperature. Another way in which fluorescence studies can be extended is by the spectrographic examination of the fluorescent light. Here especially the use of low temperatures is important as there is sometimes a striking resolution of the fluorescence bands into lines at liquid air or liquid helium temperatures. With this fine resolution it is possible to study the effects of impurities and the effect of isotopic substitution of the constituents.

In conclusion, while it is not possible over the wide field of non-destructive testing to give fully adequate illustrations, it appears that there may well be scope for the ingenious application of fluorescence methods in the field of non-destructive testing.

ACKNOWLEDGEMENTS

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The effects of penetrating radiations on materials

By S. F. PUGH, M.A., A.I.M., Atomic Energy Research Establishment, Harwell, Berks.

This paper contains an elementary account of the changes produced in solids by irradiating them with fast particles. One aspect of this work is the investigation of the properties of various types of lattice defect produced by irradiation. An advance in understanding this subject will also help in the further development of non-destructive testing techniques.

INTRODUCTION

Types of particle used in irradiation studies include neutrons, protons, electrons, deuterons and alpha particles; these are described by their mass, charge and energy, the energy being specified in electron volts per particle, a unit equal to $1{\cdot}6 \times 10^{-12}$ ergs. Gamma rays and X-rays can also cause damage in solids.

When solids are bombarded with high energy particles the following changes may be effected: (1) electrons are removed from their orbits into states of higher energy; (2) nuclear transformations occur; (3) when the moving particle comes to rest it will remain as an impurity in the solid; for example, alpha particles would become helium atoms; and (4) atoms are knocked from their lattice sites into interstitial positions. These separate effects will be treated individually in the following four sections. The fourth section is the longest since this aspect of radiation damage has received the greatest attention in recent years. In so far as the study of atomic displacements consists of a study of the properties of defects in solids it is also of relevance to the development of non-destructive testing techniques.

ELECTRON EXCITATION

The effect of raising electrons into high energy states will depend very much on the type of solid being irradiated. In insulating materials the displaced electrons may be trapped at defects in the lattice and produce changes which are more or less permanent even at room temperature. On the other hand, in metals excited electrons will rapidly dissipate their excess energy as heat and the permanent effects, if any, will arise from intense local heating in the wake of the high energy particles. Fast charged particles will dissipate a large proportion of their energy by electron excitation; for example, a 2·5 MeV charged particle would dissipate about 99·9% of its energy in this way and by transfer of energy to the atomic nuclei in amounts insufficient to cause atomic displacement.

EFFECT OF NUCLEAR TRANSFORMATIONS ON PROPERTIES

Bombardment of some materials with certain types of irradiation may result in processes in which most of the changes in properties are due to nuclear transformations rather than electron excitation or direct atomic displacement by the bombarding particle. For example, slow neutrons do not cause atomic displacement and any effect they have on properties will be due to nuclear transformations. A number of materials absorb slow neutrons readily and either are converted to higher isotopes or by subsequent decay are transmuted to a different element; for example, gold becomes transmuted to mercury fairly rapidly by irradiating with thermal neutrons in a nuclear reactor. In heavy elements absorption of slow or fast neutrons may cause the nucleus to split approximately in half—a process known as nuclear fission.

Most nuclear transformations are accompanied by a large release of energy; the fission of a uranium atom by a slow neutron is a good example of practical significance. When a uranium atom undergoes fission about 160 MeV of energy is released as kinetic energy of the fission fragments. Calculations indicate that a pair of fission fragments in uranium metal would displace about 10^5 atoms by primary and secondary collision.(1) Since the range of the fragments is short most of the damage occurs within the material in which they are formed. In the early stages of irradiation the changes in physical and mechanical properties of uranium due to fission are qualitatively similar to those in non-fissile metals.

At later stages the presence of large quantities of inert gases which form about 10% of the fission products may cause swelling or cracking. A large local release of energy due to fission fragments may in itself cause changes in properties due to the local expansions and contractions in the metal. In uranium metal the stress due to local expansion at the surface of a cylinder 300 atoms in radius co-axial with the track of a fission fragment would be about 10 tons/in.^{2} The lifetime of the fission spike is about 10^{-10} s. Prediction of local effects, therefore, depends on knowledge of the effect of high rates of stressing on plastic processes.[2]

CAPTURE OF THE BOMBARDING PARTICLE

Bombardment of solids with alpha particles has been used to introduce helium into the surface layers. This technique can be used either as a preliminary stage to study diffusion of inert gases in solids or to find the effect of the presence of inert gas on the structure and properties of the solid which is bombarded. The passage of each energetic particle will introduce a large number of displaced atoms and the effect of these must also be taken into account.

ATOMIC DISPLACEMENT

This section is subdivided into three sections describing (*a*) the interaction of radiation with matter to produce displaced atoms, (*b*) the recovery processes which modify and eventually remove completely the damage introduced by irradiation, and finally, (*c*) the effect of the presence of lattice defects introduced by irradiation on the physical and mechanical properties of solids.

It is desirable to treat recovery processes at an early stage since many of the primary defects are mobile at temperatures as low as 40° K. The types of defect remaining at room temperature, would therefore in many cases be unlike those introduced directly by irradiation. For example, in metals point defects may migrate to form platelets or clusters.

The third section treats of that aspect of irradiation studies of most relevance to advances in non-destructive testing. The treatment here is by no means complete but consists of a selection of some of the more interesting techniques which have been developed in studying radiation damage.

Description of displacement processes. Early study by Rutherford of the interaction of fast particles with matter was directed to explaining quantitatively the scattering of the incident particles rather than to measuring changes in the irradiated solid. It was found that the distribution of scattered particles could be explained by assuming that most of the mass of an atom was concentrated at a centre called the nucleus which was only about 10^{-12} cm in diameter, the diameter of an atom being about 10^{-8} cm. The nuclear charge is balanced by electrons outside the nucleus and the electrostatic field of an atom can be considered to be that due to the nucleus screened by the surrounding electrons.

When a fast moving charged particle enters the electrostatic field of an atom there is an interaction, the particle is deflected and the nucleus receives an impulse. If the atom is sited on a regular lattice point in a crystalline solid the impulse may be sufficiently large to eject the atom, perhaps stripped of some of its outer electrons, into an interstitial position between the normally occupied lattice sites.

By taking a suitable model for the atom or an expression for the electrostatic field due to an atom, it is possible to calculate the number of atoms displaced in a solid by a given incident charged particle. The calculation involves first an estimate of the rate at which energy is transferred to electrons since this process accounts for most of the loss of energy. The remaining energy is dissipated by interaction with the electrostatic field of atoms. Some of these interactions will transfer sufficient energy to displace atoms from their lattice sites. The displaced atom or ion may have sufficient energy to displace in turn other atoms and the chance of such collisions taking place towards the end of the track of the ion is estimated to be so high that one atom is ejected for every interatomic distance traversed by the moving atom or ion.[3]

With fast neutrons moving through solids interaction with electrons is negligible. Elastic collision of fast neutrons with the nucleus will produce high velocity ions. The main calculation is therefore concerned with estimating the subsequent behaviour of these ions after ejection from their lattice sites. Each displaced atom will eject about 20 atoms in subsequent collisons. In calculations of this type Seitz[1] has shown that a 2 MeV neutron in being brought completely to rest would displace 6030 atoms in aluminium, a 20 MeV proton 79 atoms and a 5 MeV alpha particle 59 atoms.

Collision calculations can also be used to indicate whether the damage in the form of displaced atoms can be considered to consist of isolated interstitials and vacant sites or whether the damage is in the form of clusters of such defects. If the clusters of interstitials and vacancies are sufficiently concentrated the arrangement of point defects will be unstable and only long range disorder will remain.[3] The energy released locally may itself be sufficient to cause some annealing within the cluster although the temperature of the surrounding metal is lower than that at which the defects are mobile. The depth to which particles of a given type and energy will penetrate in solids can be calculated. Penetration depths can also be measured directly by experiment. The penetrating power of charged particles in solids is low since they rapidly transfer their energy to electrons. 1 MeV alpha particles, protons and deuterons penetrate about 10^{-4} cm in aluminium, while 1 MeV electrons penetrate 70×10^{-4} cm. Fission fragments in uranium penetrate 4×10^{-4} cm. Fast neutrons, on the other hand, penetrate many centimetres in solids since they interact only by direct collision with the nucleus and the latter has a very small cross-section compared with the cross-section of an atom.

In calculations of the numbers of atoms displaced during irradiation it is necessary to have a value for the minimum energy—known as the threshold energy for displacement—which must be transferred to an atom to eject it from its lattice site in a solid. This threshold energy is about 25 eV, but will vary with the direction of ejection[4] and the thermal energy of the atom at the time of the collision. There may also be positions such as grain boundaries, where the energy required for displacement is less than in the regular lattice. These refinements have been investigated theoretically but so far have not been subjected to experiment.

The incident massive particle must have energy greater than E_T before it can transfer the amount of energy E_D needed to cause a displacement in a two-body collision where:

$$E_D = \frac{4M_1M_2}{(M_1 + M_2)^2} E_T$$

and M_1 = mass of moving particle
M_2 = mass of atom in solid bombarded
E_D = maximum energy transferred by a head-on collision.

Note that when $M_1 = M_2$, $E_D = E_T$.

Example of threshold radiation energies for displacements with $E_D = 25$ eV are quoted from Kinchin and Pease.[5]

Threshold radiation energy for displacements with $E_D = 25$ eV

atomic weight of stationary atoms	10	50	100	200
bombarding particles				
neutrons, or protons (eV)	76	325	638	1263
electrons, or gamma rays (MeV)	0·1	0·41	0·68	1·10
alpha-particles (eV)	31	91	169	325
fission fragments (eV) in uranium	85	30	25	27

The energy of bombarding particles is usually much greater than those shown in the table. The threshold energy for displacement in copper,[6] nickel[7] and germanium[8] has been measured experimentally by finding the minimum energy of incident particles that give a measurable change in some physical property. The values found from these measurements are in fair agreement with those predicted theoretically.

The time of interaction between a fast moving charged particle and an atom is so short that during the collision the forces holding the atom in position in the lattice can be neglected. These forces will, of course, modify the subsequent behaviour of the atom. Also for a fast moving particle the cross-section for a displacement collision with an atom is so small that the chance of striking more than one atom simultaneously is negligible; only two-body collisions have therefore been considered. For slow moving ions the latter simplification may no longer hold, and three-body collisions may be important.

It should be emphasized here that this subject is still developing and it must not be assumed that the simple picture of displacement of atoms by collision has been definitely established. A mechanism has been postulated in which the local heating disorders small volumes of crystal lattices.[9]

Recovery processes. The structure of an irradiated solid is modified by a series of recovery processes unless the irradiation is at such low temperatures that the defects introduced by irradiation are not mobile. In metals, for example, it may be necessary to irradiate at temperatures of about 10° K to retain the primary damage.

A displacement collision in a metal will produce an interstitial atom and a vacant lattice site. Either of these point defects can migrate through the lattice if the temperature is sufficiently high, and if they meet they will be mutually annihilated. Alternatively they might diffuse away to other metastable positions of lower free energy. The positions of lower energy are called "sinks" and examples of these are grain boundaries, phase boundaries, clusters of interstitials or vacancies, impurity atoms or dislocation lines. Annealing at a higher temperature will allow a captured interstitial or vacancy to diffuse to sites of still lower energy and finally to be removed completely by processes of self-diffusion. Defects in a metal alters the electrical resistance and so measurements of resistance can be used to indicate their presence. Changes in the resistance on subsequent heating can be used to indicate the rate at which annealing is taking place. In an experiment of this type Cooper, Koehler and Marx[10] showed that when copper was bombarded near 10° K with 12 MeV deuterons the primary damage could be retained, but at 40° K a sharp drop in resistance indicates that the first annealing stage has been reached. There follows a range of temperature in which annealing is slow and then a second sharp annealing stage is found at −30° C with an activation energy of about 0·7 eV. There is at present a considerable amount of research in progress to identify the nature of these annealing stages by measuring changes in physical properties, such as stored energy, during the annealing stage and by comparing the properties of the defects migrating during these annealing stages with those in similar annealing stages found in cold worked and quenched metals. The interpretation of these results is still controversial since the number of possible annealing processes is very large and effects due to interaction of point defects with impurities and other lattice defects complicate the interpretation.

Changes in physical and mechanical properties. Interstitials and vacancies in a metal scatter electrons and so increase the electrical resistance. Measurement of the change in resistance due to irradiation could be used to measure the number of defects present if the effective scattering due to each kind of defect were known. Calculations have been made to evaluate the increase in resistance of copper due to the presence of 1% vacancies and 1% interstitial atoms; a number of conflicting results have been published. Calculations of stored energy due to the presence of point defects are probably more reliable but the measurement of stored energy in irradiated metals is a very difficult matter since the amount stored is small. Overhauser[11] has measured the ratio of stored energy to electrical resistance change for the annealing stage in copper at −30° C in the hope of identifying the nature of the defect migrating during this annealing stage.

With semi-conductors it is possible to achieve more by direct experiment since the electrical properties of the interstitials and vacancies introduced by irradiation are similar to those of impurities in that both act merely either as electron traps or donors.[12] By comparing the effect of controlled additions of impurities with the effects of measured doses of irradiation it is possible to determine the number of defects introduced by a given amount of irradiation. The results can then be compared with the calculations on the basis of collision theory. There is an uncertainty to a factor 2 in this analysis since it is not clear whether the minimum in conductivity would occur when one electron is trapped per interstitial vacancy pair or whether it would occur when two were trapped.

Graphite is capable of storing displaced atoms formed by irradiation to a very high concentration at room temperature, causing changes in lattice parameter of more than 1%, the expansion along the c axis being greater than that along the a axis.[13] The concentration of point defects produced by irradiation in graphite has been measured by Antal, Weiss and Dienes[14] using the new technique of slow neutron scattering. This method uses neutrons of wavelength too long to give Bragg reflexions. Vacancies and interstitials scatter under these conditions by equal amounts. The method is particularly successful in graphite where the scattering due to other causes is very small, but it is not certain what effect clustering of the defects has on the results obtained.

In the absence of recovery processes the continued production of displaced atoms by irradiation would eventually so obliterate the crystalline structure that it is no longer useful to picture the structure as a lattice containing defects but rather to consider the structure as amorphous. Some minerals containing thorium and uranium are 10^9 years old and have been converted to an amorphous state by disintegration of the thorium or uranium. These minerals can be used to demonstrate in a spectacular way the phenomenon of stored energy due to lattice displacements. Berzelius[15] in 1815 showed that when gadolinite was heated slowly there was a marked release of energy which was sufficient to raise the temperature by about 800° C.

In non-metals thermal conductivity at very low temperatures

can be used to indicate the presence of single or clustered point defects and long range defects. The interpretation of these measurements is rather complex and is still in dispute, but the work so far has led to some useful advances in the theory of thermal conductivity.

Irradiation of alkali halides causes changes in colour.[16] The colour centres have not been definitely ascribed to the production of displaced atoms by irradiation since they might also be due to excited electrons trapped at pre-existing defects. The difficulty in interpreting subsequent annealing behaviour is in distinguishing between electronic and ionic processes when the activation energies for both processes are almost equal.

In solids consisting of more than one kind of atom arranged in an ordered array on a lattice, irradiation can produce disordering by displacing atoms. Effects of this kind have been studied using ordered alloys such as Cu_3Au and CuAu. The magnitude of the disordering is greater than that deduced from collision theory. Seitz[17] therefore suggested that the extra disordering arose from the plastic deformation caused by local heating in the path of the bombarding particle. Kinchin and Pease[18] have suggested an alternative explanation based on "replacement collisions." The latter are thought to take place when a displaced atom still possessing some kinetic energy but less than the displacement energy forces another atom into an interstitial position and takes up the vacant site created. A chain of replacement collisions in an ordered alloy would leave a row of disordered atoms. Collisions of this type were neglected in earlier calculations. Migration of interstitialcies by thermal activation can cause disordering in a similar manner. The number of disordered atoms per defect would therefore depend on the mean free path of a defect before trapping.[19]

In a solid consisting of more than one phase, irradiation may produce mixing at the phase boundaries. The importance of this effect will increase as the particle size distribution of the two phases decreases but it is usually negligible. Recovery processes would in any case tend to remove changes of this kind, since the diffusion distances are small.

Finally the effect of irradiation on the mechanical properties of metals will be described. Irradiation of metals with particles sufficiently energetic to displace atoms raises their yield stress[20] in a manner somewhat similar to alloying copper with zinc; the magnitude of the effect increases with the integrated irradiation dose. The slip bands take on a similar clustered appearance.[21] In metals which show a brittle-ductile transition, the transition temperature can be raised by as much as 100° C by fast neutron bombardment;[22] the latter effect is of considerable practical significance.

The interstitials and vacancies in an irradiated metal probably do not have their maximum effect on the mechanical properties when they are in their initial randomly dispersed state. The changes in mechanical properties arise from interaction between defects introduced by irradiation and dislocations already existing in the metal. It is thought that the defects either form clusters near the dislocations which retard their movement in a manner similar to that of the nuclei formed in an age hardening alloy or they migrate to the line of the dislocation and form jogs upon it.[23] Internal friction measurements can be used to demonstrate the pinning of dislocations in an irradiated metal. There is a drop in the damping capacity after irradiation.[24]

The change in mechanical properties anneals out at a temperature similar to that for annealing cold work and the activation energy in cases where it has been measured is equal to the activation energy for self-diffusion. The point defects introduced by irradiation become mobile at much lower temperatures and have lower activation energies. The distribution of defects causing a change in mechanical properties is therefore a fairly stable intermediate state.

CONCLUSIONS

A study of irradiation damage has stimulated interest in the properties of defects in solids as, for example, their free energy, mobility, electrical resistance, optical properties and effects on mechanical properties. This study is still at an early stage and has shown to be very complex. There have, however, been some successes and the results of these investigations should provide useful information concerning the relationship between internal structure and physical and mechanical properties which should be of interest and stimulate further developments in non-destructive testing techniques.

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Physical methods in medical diagnosis

AN EVENING DISCOURSE DELIVERED DURING THE BRISTOL CONFERENCE

By Prof. C. B. Allsopp, M.A., Ph.D., D.Sc., F.Inst.P., Guy's Hospital Medical School, London, S.E.1

An account was given of a number of modern methods used in medical diagnosis which depend on adaptation of simple physical apparatus and principles. The lecture was illustrated by reference to ballistocardiography, thermometry, the stethoscope, electromyography, the strain gauge and xeroradiography. It was stressed that physics as applied to medicine is, fundamentally, the same physics as is practised in non-destructive testing or in any industrial research laboratory.

The growing willingness of medical men to invite and to accept the help of physicists in the solution of their problems is no new phenomenon. Since the time of Galileo, who was a student of medicine, individual physicians have interested themselves in physics and physicists in physic; but it is perhaps true to say that, until comparatively recently, the contributions of the physicians to physics outweighed those of physics to medicine. To give but three examples: modern electrical theory is largely based on experiments described by William Gilbert in his book, *de Magnete*, which appeared in 1600. Gilbert was personal physician to Queen Elizabeth I. Secondly, Thomas Young (1773–1829), on whose work the wave theory of light was ultimately established, practised medicine in Welbeck Street, London. Thirdly, a considerable contribution to the development of the general principle of the conservation of energy was made by a German physician named Meyer, who based his conclusions on the interconvertibility of the various forms of energy on observations on the blood of the Javanese. Only now, in the contemporary collaboration of physician and physicist, is some of this debt beginning to be repaid.

I would like to start this lecture, therefore, with a plea that this common interest may be stimulated and developed. I cannot do it better than by quoting from a distinguished physician, Richard Mead (1673–1754) who was executor to Thomas Guy, the founder of the hospital in which I have the privilege of working. In the preface to *A Mechanical Account of Poisons* (1702) he wrote:

"It is very evident, that all other Methods of improving Medicine have been found Ineffectual, by the Stand It has been at these Three or Four Thousand Years; and that since of late Mathematicians have set Themselves to the Study of It, Men do already begin to Talk so Intelligibly and Comprehensibly, even about abstruse Matters, that it may be hoped in a short Time, if Those who are Designed for this Profession, are early, while their Minds and Bodies are Patient of Labour and Toil, Initiated in the Knowledge of Numbers and Geometry, that Mathematical Learning will be the Distinguishing Mark of a Physician from a Quack; and that He who wants this necessary Qualification will be as Ridiculous as One without Greek or Latin."

A similar plea was made by John Quincy (*d.* 1722) in his *Lexicon Physico-medicum*:

"I say Physics and Medicine, because the latter cannot subsist without the former; . . . The Reader therefore on this View, will not wonder to find in a Work under this Title, a great deal about Attraction, the Laws of Motion, Gravitation, Air, Winds, Tides, Light, Heat, Cold, and the like; because he will find how they naturally lead to the Knowledge of some important Points of Practice, which, without such previous Lights, must lie intirely in confusion, and upon the Hazard of Experiment and Guess-work.

"And because what is brought from Physics and Mechanics takes up so much Room here, it may be necessary to inform the Reader, that there is no Knowledge in Medicine but by such Means."

It is not possible, in the space of one hour, to do more than describe a few of the contacts of physics with medicine which have come to my personal notice, but before I do so let me show one very early example. This is a multiple-purpose bed, Fig. 1, which was described by Santorio

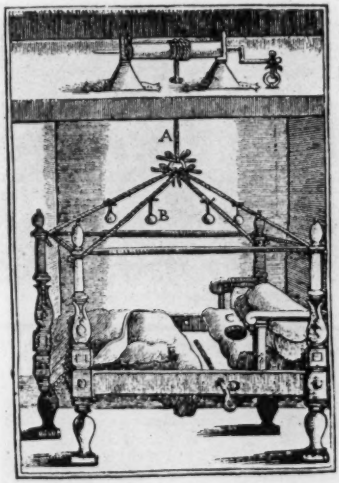

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Fig. 1. Santorio's multiple purpose bed (1623)

(1561–1636) in a *Commentary on Avicenna* (1623). It has a number of advantages over the ordinary bed: it can be used also as an armchair, it is fitted to take a bed table, it can be suspended off the ground, and when so suspended "sweet music" made by the collision of the hollow spheres *B* would lull the patient to sleep. Thus, mechanics, acoustics and light engineering were applied to the healing of the sick.

THE BALLISTOCARDIOGRAPH

My first modern example is also a suspended system, namely the ballistocardiograph, Fig. 2, an apparatus which applies the elementary principle of the ballistic pendulum to investigate the functioning of the heart muscle. It has a

great advantage over other methods in that all that is required of the patient is to lie on a suspended couch and to relax, without any need for attaching electrodes or other manipulation. The couch *C* in Fig. 2 is made rigidly of a honeycomb (aeroplane wing) construction, and is suspended from blocks in the ceiling by four piano wires *W* just strong enough to take the weight of an average patient. The natural oscillations

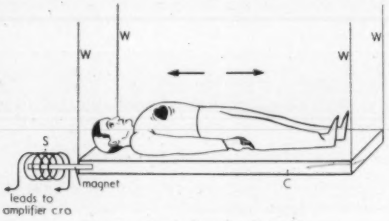

Fig. 2. The ballistocardiograph

of this suspended system, which differ greatly in period from the heart frequency which is to be observed, are minimized by suitably positioned dashpots. Extraneous vibrations, e.g. from traffic, are adequately damped out by winding string round the piano wires.*

Attached to the side of the couch is a small bar magnet *M* which projects into a solenoid *S*. The rhythmic thrust produced by the contractions of the heart muscle cause minute longitudinal movements of the couch, the resultant oscillations having an amplitude of the order of 1 mm. This is sufficient to produce in the solenoid an electromotive force which can be amplified, displayed on an oscillograph screen, and recorded. One such record, or "velocity trace," normal for a young person, is shown in Fig. 3(*a*). The maximum

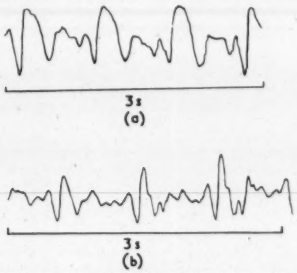

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Fig. 3. The ballistocardiograph: (*a*) velocity; (*b*) acceleration trace

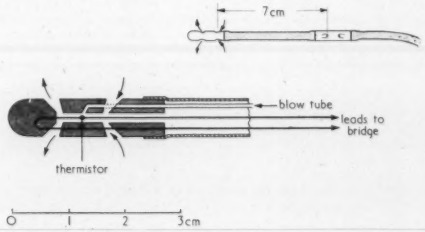
amplitude of the electromotive force, which repeats at approximately 1 s intervals (pulse rate) shows a very slight periodic rise and fall over about 3 s intervals. This appears to be the effect of respiration (frequency *c.* 20 per second).

The lower record in Fig. 3 is an "acceleration trace" which is recorded directly from the oscillation of the couch by means of an electronic differentiator. This trace, of course, gives a direct measure of the heart thrust and is the significant one for purposes of clinical diagnosis. The physics problem involved is to convert the velocity trace, Fig. 3(*a*), into the acceleration trace, Fig. 3(*b*), without addition of "noise." The correspondence of the detail of the two traces shows that this can be achieved to such a degree that the clinical features are not confused during the recording.

THERMOMETRY

I turn next to one of the best known—though not really so very old—diagnostic instruments, the thermometer. The first description of a thermometer designed for measuring body temperature was made by Santorio, in a *Commentary on Galen* (1612), but it does not appear to have been widely used. A further description was given in Boerhaave's *Aphorisms* (1709), but another 150 years elapsed before thermometry became at all general in medical practice. In 1859, the clinical use of a thermometer was described in *Ratio medendi* by De Haan who has been described as the physician "who introduced the thermometer into the observation of the sick." The first full account of clinical thermometry was given by Wunderlich in *Das Verhalten der Eigenwärme in Krankheiten* in 1868. The use of the short self-registering type of clinical thermometer appears to date from about 1867 and has been associated with the names of the clinicians Sir W. Aitken and Sir C. Allbutt.

It is interesting that after Sir Humphry (then Mr.) Davy had discovered the properties of nitrous oxide, he was employed at the Pneumatic Institution at Bristol by Dr. Beddoes, who ordered him to treat a paralytic patient with the new gas. Davy is stated to have "inserted a small



(*a*)

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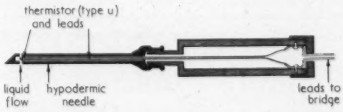

(*b*)

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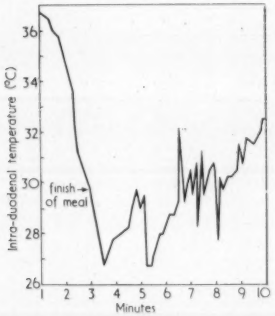
Fig. 4. (*a*) Thermistor mounted in a plastic tube for insertion in the alimentary canal. (*b*) Thermistor mounted in a hypodermic needle

* The principal features of the ballistocardiograph were illustrated by means of a short film sequence.

pocket thermometer under the tongue of the patient" before starting the administration. This must have been between 1799 and 1801. A description of a 5 in. portable thermometer was published in 1800 in the *Medical and Physical Journal*.

Convenient as the clinical thermometer is, it has obvious disadvantages. For some time, thermocouples have found a use in medicine, both because they can record continuously, and because they can measure temperatures at a point, e.g. thermocouples have been used to measure differences of temperatures between normal and "scar" tissue after operation or grafting in order to follow the return of the latter to normal. The recent introduction of the thermistor, however, has provided a far more powerful tool. The tiny bead of metallic oxides, whose resistance varies rapidly with temperature, can be mounted in such a way that it can be inserted into body cavities, and connected by fine leads in one arm of a balanced Wheatstone bridge. Any variation in temperature is then indicated by, and measured in terms of, the off-balance current of the bridge. Fig. 4(*a*) shows a thermistor mounted in a small plastic tube which can be swallowed and moved into various parts of the alimentary system,[1] and Fig. 5(*a*) is a record so obtained of the variations in the stomach temperature of a subject who was eating an ice-cold meal. Alternatively, two thermistors can be mounted at a known distance apart—the time interval between the passage of food past each of them in turn is measured, and can then be used, for example, to investigate obstructions. The flow of a liquid meal through a subject's oesophagus is illustrated in Fig. 5(*b*). Another use for a single thermistor is illustrated in Fig. 4(*b*). Here the thermistor is set in a hypodermic needle for insertion into a great blood vessel. If it is heated by a small current above the temperature of its surroundings, the rate at which blood flows over it can be deduced from the rate at which the thermistor cools, which can be deduced in turn from observation of the off-balance current of the bridge.



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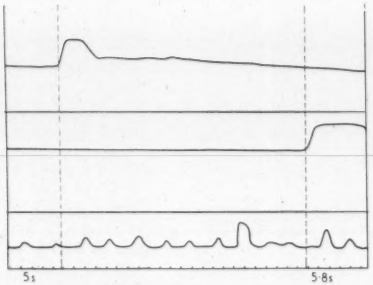

(*b*)

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Fig. 5. (*a*) Thermistor record of fluctuations of intra-duodenal temperature in a subject eating an ice-cold meal. (*b*) Schematic reproduction of part of a dual thermistor record of the passage of food through the oesophagus. Upper curve: proximal thermistor; middle curve: distal thermistor; bottom curve: respiration

THE STETHOSCOPE

Another familiar diagnostic aid is the stethoscope. This instrument was first described by Laënnec in 1819. In its earliest form it consisted only of a hollow wooden tube. That shown on the right in Fig. 6, now in the Gordon Museum at Guy's Hospital, was one of the first of Laënnec's pattern to be used in this country. It has a detachable brass chest piece. According to Sir Samuel Wilks, it dates from before 1826, in which year Laënnec died. It was presented to Thomas Hodgkin (who first described what is now known as Hodgkin's disease) when he was on a visit to Paris, and was used both by him and by Wilks. The more elegant model shown on the left is also in the Gordon Museum and also belonged to Wilks. A binaural type, with rigid tubes, was introduced in 1829, and flexible tubes appeared in 1855. The use of a rigid diaphragm in the chest piece to facilitate the hearing of cardiac sounds dates from 1901.

[Reproduced by permission of the Curator of the Gordon Museum]

Fig. 6. Early stethoscopes, *c.* 1826

Recently, in the course of carrying out audiometry on patients suffering from a certain form of deafness, it was convenient to use a stethoscope tube in reverse and to feed

the audiometer tone into the patient's ear through it. This necessitated an investigation of the acoustic properties of a flexible tube. It proved to be very "deaf." Fig. 7(*a*) is a typical audiogram for a deaf patient whose hearing of frequencies above 3000 c/s is deficient: Fig. 7(*b*) shows the

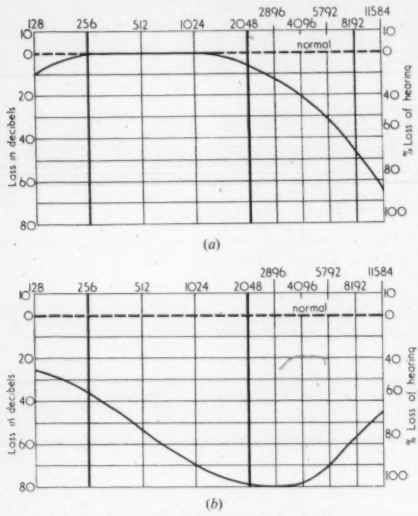

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Fig. 7. (*a*) Typical audiogram for a deaf patient. (*b*) "Audiogram" for sounds transmitted through a flexible rubber tube

has had to pass through a layer of inhomogeneous, non-rigid, material.

ELECTROMYOGRAPHY

Electrophysiological phenomena have been utilized in diagnosis for many years, and I would like to mention one particular application, electromyography. When a muscle contracts, electrical waves pass along each fibre. Their amplitude is of the order of a few microvolts and their frequency several hundred cycles per second. These electromotive forces can be picked up either by surface electrodes which are attached to the skin above the muscle by suction, or by needle electrodes which are inserted into the muscle itself, and are then amplified to be displayed visually on the cathode-ray screen, recorded on a magnetic memory or with a pen recorder for future reference, or converted into audible signals. When surface electrodes are used, the recorded discharges are very complex since many units, each containing numerous fibres, contribute to them. With a muscle at rest, only the "noise" from the amplifier is seen or heard. As it is voluntarily contracted by the subject, the amplitude of the signal on the screen increases and the sound record rises in a crescendo to a crackling roar so long as the muscle is active. These phenomena have been used, for example, in a study of the muscles involved in posture,[2] i.e. those which act to maintain a standing person in equilibrium.*

Clinically the electromyograph is used in the diagnosis of injury to muscle or to the corresponding motor nerve. For this purpose needle electrodes are used. The following typical recordings illustrate the method. Fig. 8(*a*) shows a *normal* motor unit potential. Its duration is 5 ms. It was picked up from a single motor unit in the forearm muscle of a patient who was making a weak voluntary effort to contract the muscle. This action potential is the sum of the individual contributions of the many fibres which make up one motor unit, "firing" almost simultaneously. In Fig. 8(*b*), the patient was making a stronger effort: a large number of motor units throughout the muscle mass are brought into play, and the summation of their individual action potentials gives this

(*a*) (*b*) (*c*) (*d*) (*e*)

Fig. 8. Electromyography

(*a*) A normal motor unit potential, duration 5 ms: weak muscular effort.

(*b*) Normal "interference pattern" from a large number of motor units: stronger muscular effort.

(*c*) An abnormal motor unit potential, regeneration of motor nerves after damage.

(*d*) An abnormal single fibre potential, duration 1·5 ms: denervated muscle.

(*e*) An abnormal burst of potentials: excessive excitability.

corresponding curve for the sound transmitted through the flexible tube. An interesting feature is the increase in response at higher frequencies, at which, of course, the tube is most probably acting as a resonator. The question may well be asked whether the sounds a doctor hears through a stethoscope are really the true sounds; and it must be remembered as well that before a heart or chest sound reaches the stethoscope it

complex "interference pattern." The wave forms recorded in Figs. 8(*a*) and 8(*b*) are both normal; that in Fig. 8(*c*), however, is abnormal and complex, by comparison with 8(*a*):

* A section of a sound film entitled "Electromyography of Postural Muscles," by Dr. J. Joseph and Mr. A. Nightingale, was shown at this point in the lecture.

it is associated with the regeneration of motor nerves after damage. Fig 8(*d*) shows the abnormal potential from a single muscle fibre. Compared with Fig. 8(*a*), it differs essentially in its short duration, which is 1·5 instead of 5 ms. Such discharges are given by denervated muscles, i.e. those in which voluntary control has been lost through severance of or damage to the motor nerve. Finally, Fig. 8(*e*) records a burst of potentials following each other very rapidly. Such bursts occur in response to a mechanical stimulus and indicate excessive excitability of the nerve or muscle fibres.

These abnormal visual patterns are, of course, transient and are seen on the oscillograph screen against a general background, so that they are not always readily recognisable. Converted into sound, however, they can give rise to quite characteristic sound patterns. Thus, the abnormal single fibre potentials [Fig. 8(*d*)] give a "tap-tap" noise resembling that from a two-stroke motor cycle engine; and bursts such as those in Fig. 8(*c*) cause a scream only too reminiscent of that of a diving dive-bomber. They can thus be recognized at once by ear, even against the background "roar" from the general muscle activity.*

Myoelectric potentials generated in an amputation stump have been used successfully to operate an artificial "limb" consisting of two hooks arranged to represent a thumb and an index finger.[3] This application is complicated, since the signal levels from the controlling muscle differ during the various stages of initiating, maintaining and releasing the grasp, Fig. 9, and its further development requires the collaboration of an engineer familiar with micromotors and their ancillary apparatus.

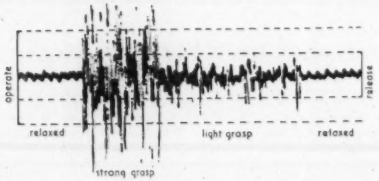

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Fig. 9. Electromyograph signal levels during initiation, maintenance of and release of grasp between thumb and index finger

THE STRAIN GAUGE

An engineer's tool which has recently found an interesting application, though dental rather than medical, is the strain gauge. It is being used to measure the thrust developed by the molars while the subject is chewing.[4] For this purpose, the gauge is mounted in a cap, Fig. 10(*a*), which is then inserted in an inlay in the tooth, Fig. 10(*b*)—the experiments naturally being made with the collaboration of patients undergoing dental treatment. The strain gauge, like the thermistor, is connected into a balanced, calibrated, Wheatstone bridge and thrusts can be read directly from the off-balance current produced when a stress is applied. Fig. 11(*a*) shows the thrusts exerted by a person chewing a soft meal, and Fig. 11(*b*) also contains a synchronized electromyograph record of the activity of the jaw muscle. The very large disturbance in the electromyograph record was caused by the patient swallowing.

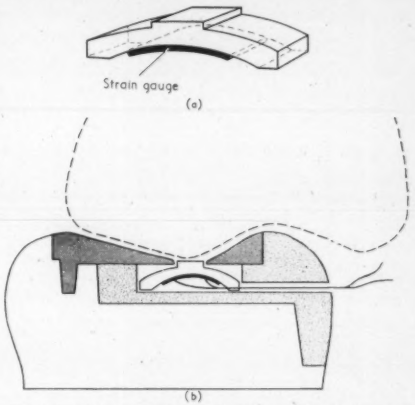

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Fig. 10. (*a*) Strain gauge mounted in a cap for dental use. (*b*) Cap and gauge built into inlay in tooth

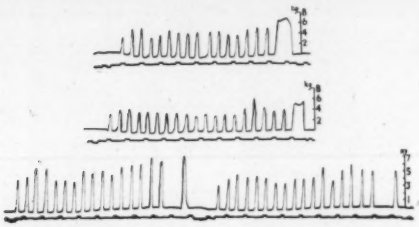
XERORADIOGRAPHY

I must now turn to a type of investigation which was, until recently, the sole interest of this Group of the Institute: *viz.* radiography. It has been said recently that, *in principle*, radiography has not made any advance since Röntgen discovered X-rays: its progress has been entirely technical. Whether the new method to be described, xeroradiography, contradicts this entirely may be doubtful, but it certainly invokes a new principle in its method of recording the radiographic image.[5] When X-rays fall on the charged surface of a suitably-prepared amorphous selenium plate, charge leaks away from any given point in proportion to the quantity of radiation falling on it, so that an electrical image is formed on the plate. This image can be developed by dusting the plate with a fine powder, electrically charged, which adheres to the surface again in proportion to the charge density.

Figs. 12(*a*), (*b*) and (*c*) show how this is achieved in a prototype apparatus made by Ferranti Ltd. Fig. 12(*a*) shows the selenium plate being charged with electrons from a point raised to 1500 V. In Fig. 12(*b*) the plate is being exposed in its cassette in the conventional way. Development is shown in Fig. 12(*c*). Ordinary face powder is dusted on to the surface of the plate by the agitation of the diaphragm of a motor horn, and is charged positively or negatively (according to whether a negative or positive radiograph is desired) *en route*. After use, the powder is wiped off the selenium surface with a soft cloth, and residual charge is removed by exposing it to strong light for a few seconds. The time required to make a radiograph in this way is less than 1 min, and the whole process is dry and requires no dark room.

If a permanent record is required, of course, further processing, e.g. photography of the radiograph, is necessary, and this

* A sound film sequence was shown to illustrate these wave patterns and their associated noises.



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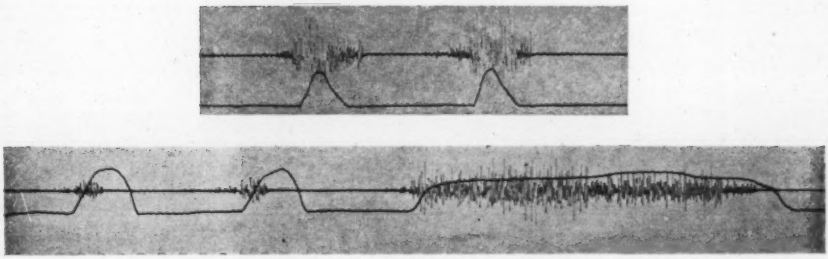

(*b*)

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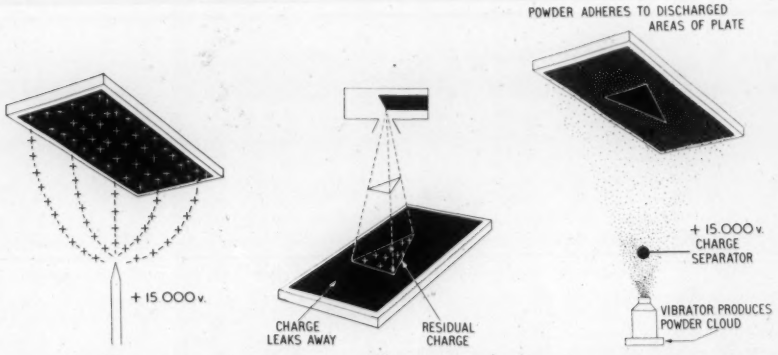
Fig. 11. (*a*) Calibrated strain gauge record of the thrust developed by molars of a person chewing a soft biscuit.
(*b*) Strain gauge records with simultaneous electromyograph records



(*a*) (*b*)

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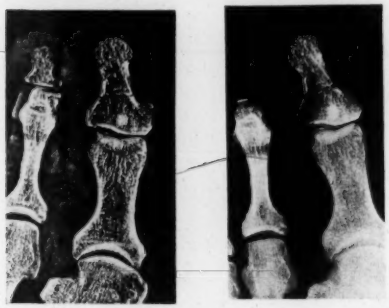
Fig. 12. Xeroradiography

(*a*) The selenium plate is charged by electrons streaming from a point.
(*b*) The plate is exposed in the normal way.
(*c*) The plate is developed by dusting with charged powder.

is one of the major obstacles to the clinical use of the method. The other is that the exposure time required, at present, is very much longer than that for conventional X-ray film, although the selenium plate has a far greater tolerance as can be seen in Fig. 13, so that a patient receives more radiation. Neither of these difficulties, however, is so serious in non-clinical applications of the process.

Four typical xeroradiographs, side by side with conventional radiographs, are reproduced in Figs. 13(*a*), (*b*), (*c*) and (*d*). The greater exposure tolerance of the plate results in detail remaining visible in the xeroradiograph which would have been obscured by over-exposure on a conventional film, e.g. the hyoid and the air passage in Fig. 13(*b*). Similarly, in Fig. 13(*c*), the plate was deliberately under-exposed but still reveals the detail required by the surgeon. A feature of xeroradiographs is that the powder tends to collect along and to emphasize boundaries. This is useful for fractures as can be seen in Figs. 13(*a*) and (*c*).

Finally no account of physical methods in medical diagnosis would be complete without at least a reference to the use of radioactive isotopes. As in industry, their use as tracers is proving invaluable. To give two examples out of many, the use of iodine in investigations of thyroid function and of sodium in plastic surgery* are now routine procedures. There is no doubt that in this by-product of the application



(*a*)
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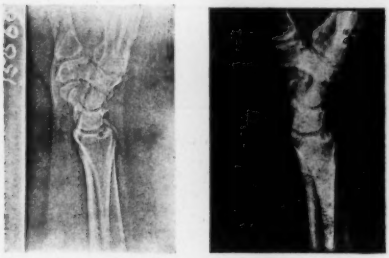

(*c*)
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(*b*)
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Fig. 13. Xeroradiographs (right) compared with conventional radiographs (left)

(*a*) Antero-posterior view of a toe showing a fracture through the distal phalanx.

(*b*) Lateral view of a normal cervical spine. Note the clarity of the hyoid bone and the air passage in the xeroradiograph.

(*c*) Lateral view of a wrist at the conclusion of treatment for fracture.

* This was illustrated by the appropriate sequence from the Crown Film Unit's "Atoms for Peace" film.

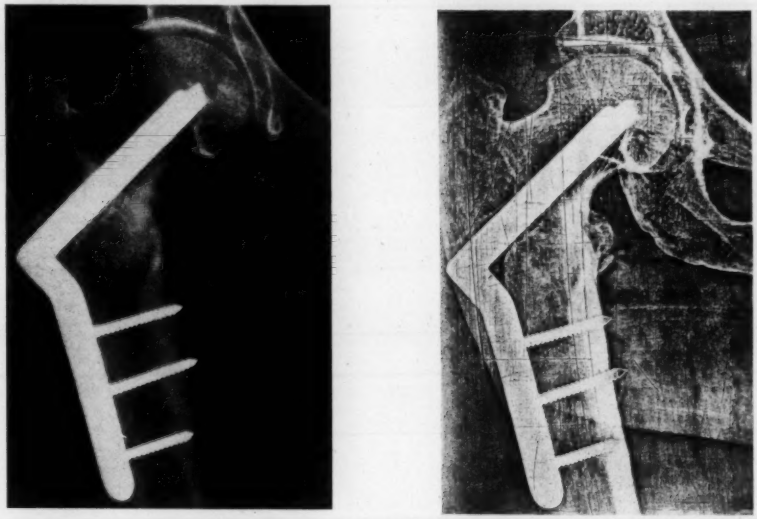
of atomic energy, physics has placed in the hands of the physician, if he is willing to use it, perhaps the most powerful diagnostic tool which he has ever possessed.

ACKNOWLEDGEMENTS

In preparing this lecture I have had the object of showing how ordinary physical methods are being adapted for medical purposes. It would not have been possible without the assistance of Mr. A. Nightingale, who has not only supplied much of the material but also supervised the preparation of the film strips and their associated sound tracks. It is a great pleasure to express my indebtedness to him.

I have drawn freely on an article on "Physics and Medicine" by Prof. W. V. Mayneord, and on "Historical and Bibliographical Notes" signed by "N. H. J.," in Vol. 3, No. 6, of the *British Medical Bulletin* (1945). Various colleagues at Guy's Hospital Medical School have allowed me to use their research material, in particular Dr. D. C. Deuchar, Dr. J. N. Hunt, Dr. D. J. Anderson, Mr. R. W. Stanford, Mr. R. D. Moore, Mr. C. K. Battye and Mr. R. E. George. I am grateful to all these gentlemen for their assistance.

Lastly, but by no means least, the diagrams, slides and film sequences were prepared in the Illustration and Photographic Department of Guy's Hospital. To Miss S. Treadgold and Mr. C. Engel I record my sincere thanks for much invaluable advice and help.



(*d*)

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Fig. 13. Xeroradiographs (right) compared with conventional radiographs (left)—*continued*

(*d*) Hip with plate. The exposure on the xeroradiograph was considerably reduced, but the exact position of the pin in relation to the bone is clearly shown.

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The detection of fatigue in metals

By R. F. Hanstock, Ph.D., F.Inst.P., High Duty Alloys Ltd., Slough, Bucks.

This is a brief review of the nature of fatigue and of the methods that have been employed or suggested for examining the development of this condition in metals. The primary consideration is the assessment of the potential value of these methods as primitive non-destructive tests to reveal fatigue in its least dangerous stage, i.e. prior to the development of serious structural weakness.

THE NATURE OF FATIGUE

When considering whether it is possible to use non-destructive methods to detect progress of fatigue in metals, it is necessary to start from what is known of the mechanism of fatigue. The final phase of fatigue is characterized by the formation under fluctuating stress of a brittle type of fracture, the significant feature being that this fracture occurs when the maximum of the fluctuating stress may be only a fraction, one half or less, of the normal static strength of the material. We are concerned with the processes that lead to this fracture and to a consideration of whether they are such that they can be detected non-destructively so that ultimate fracture may be forestalled by removal or preventive treatment of the part affected.

Research by many investigators over a period of years shows that the following processes are associated with fatigue:

(1) Transformation of a proportion of strain energy associated with the fluctuating stress to produce a change in condition and/or heating of the metal.
(2) Plastic deformation which, although on a minute scale during the single application of what is normally regarded as a stress within the elastic range, accumulates to a significant amount when the stress is repeated many times.
(3) Formation of small cracks which are usually of the order of 1/1000 in. in length when first observed.
(4) Growth and coalescence of such cracks to form a large fatigue crack which often has a considerable width as a result of a certain amount of the metal being ejected.

The number of stress cycles of a given magnitude to cause complete failure usually shows considerable scatter.

It appears that the ideal non-destructive test to determine the progress of fatigue would be one that is sensitive to the processes occurring before stage (3), that is, it should be based on detection of either the material's capacity for transforming mechanical energy or on detection of the deformation or some associated change in physical state that precedes the formation of a crack. If it should prove to be impossible to apply tests of this type to the practical examination of components the only alternative seems to be to devise methods that are sensitive to the detection of fatigue cracks as soon as possible after their inception.

The nature of the problem has been evident from some of the earliest investigations of the fatigue process. These showed by metallurgical techniques and microscopic examination that certain regions of the metal, e.g. individual grains suitably orientated with respect to the applied stress, develop slip bands which are often sites for the development of a crack. One well-known theory of the fatigue process (Orowan[1]) is based on the cumulative effect of the deformation and strain hardening of plastic regions in the metal until cracking occurs. Freudenthal and Weiner[2] have suggested recently that strain hardening is not an essential factor in the formation of a crack and consider that heat-bursts associated with the localized deformation may produce sufficiently sharp temperature gradients to induce thermal stresses that result in the formation of small cracks.

What is most significant for our present purpose is the realization that during the fatigue process only small isolated regions of the metal are affected and that the number of these regions may depend on the state of the metal. Hunter and Fricke[3] have concluded that the effect of alloying aluminium is not only to increase its static strength, but also to make fatigue an increasingly localized phenomenon. It is understandable that, with increasing localization of the changes that occur, the problem of their detection becomes more difficult. Recently it has been shown[4] that in a certain alloy, which is important as an aircraft constructural material, a secondary effect, namely precipitation, is associated with the cumulative plastic deformation induced by cyclic stressing. This and other secondary effects such as recrystallization[5] are of the type that are normally induced only by raising the temperature of the material in the absence of stress. The localized nature of the fatigue process is emphasized by these secondary effects, which under certain conditions can be shown quite clearly (Fig. 1).

Fig. 1. Section of a specimen of aluminium alloy D.T.D. 683 after being subjected to 26×10^6 cycles of reversed torsion producing a surface shear strain of 45×10^{-4} (equivalent to 8·5 tons/in.^{2} reversed shear stress). Section polished and etched with aqueous 25% nitric acid ($\times 500$)

Thus, a non-destructive test based on the detection of metallurgical changes in the material must be such that it is capable of responding to the characteristics of small regions where deformation or secondary effects of the type mentioned have occurred.

Tests which measure only the average properties of the material will, in general, not be sufficiently sensitive to detect the changes occurring in an amount of material which represents probably less than a fraction of one per cent of the total volume. For example, it is known that prior to the formation of a crack the fatigue process has little effect on the static strength, modulus, or natural frequency.

MECHANICAL HYSTERESIS

There is, however, one property that appears to be sufficiently sensitive to show, from an average measurement, the changes occurring in a small proportion of the whole material. This is the energy AE lost per cycle of the applied stress, i.e. the mechanical energy transformed as a result of the stress/strain hysteresis of the material. This hysteresis energy may be measured approximately as the heat generated, or in terms of the damping capacity AE/E of the material where E is the maximum strain energy of the stress cycle. As some of the hysteresis loss may be associated with change in state of the material the measurement of damping capacity is perhaps to be preferred. This is a quantity which is highly dependent on the magnitude of the cyclic stress and, at least, in certain materials, on the number of stress cycles that have been applied[4] (Fig. 2). For the particular material B.S.L. 65

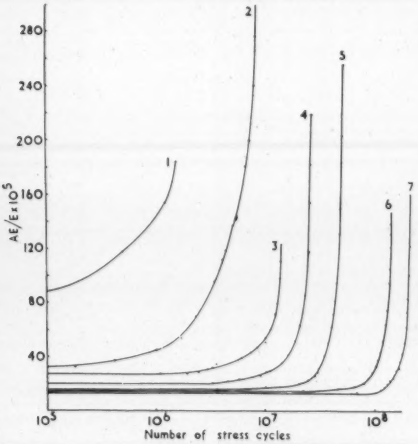

Fig. 2. Variation of damping capacity (AE/E) of the aluminium alloy B.S.L. 65 with reversed strain and with the number of cycles of reversed strain. Tested in torsion at the following levels of surface shear strain $\times 10^{-4}$; (1), 48; (2), 45; (3), 42·5; (4), 40; (5), 37·5; (6), 35; (7), 32·5

to which this figure refers, the changes in damping capacity during cyclic stressing have been associated with the secondary effect of precipitation and in another aluminium alloy D.T.D. 683, the regions of precipitation have been shown to be those where small fatigue cracks develop. For this alloy also a considerable increase in damping capacity is associated with the precipitation which is a preliminary to crack formation.

Thus, there is here, at least for some materials, a possible approach to a non-destructive method for estimating the progress of fatigue. Unfortunately it is an essential requirement that the energy loss that is measured must be substantially the hysteresis loss associated with the material. This can be very small, e.g. the damping capacity may range from 10^{-5} to 10^{-2} according to the magnitude of the stress applied. Thus it is impossible, except under certain restrictive laboratory conditions, to eliminate losses of energy that are not associated with the material and have no bearing on the development of fatigue. It does not appear that in any engineering structure it would be possible to detect incipient fatigue by these means.

DEFORMATION PHENOMENA

The methods of observation of slip bands and other deformation phenomena, such as those demonstrated by Forsythe,[5] do not appear to be applicable to the examination of normal engineering components. Changes that may be associated with the fatigue process have been observed in X-ray diffractions by Wood[6] and later by Franks and Holden,[7] but it is difficult to see how a practical non-destructive test could be developed along these lines.

Thus, the present position is that before the formation of a fatigue crack the development of fatigue can be followed in certain types of material provided that they are examined in suitable forms under laboratory conditions. However, the restrictions imposed by the form of test material or its preparation for examination during the test are such that a practical non-destructive test has not been devised.

DIMENSIONAL EFFECTS

From time to time other possible methods of detecting the progress of fatigue of metals have been suggested. According to Rosenfield and Averbach[8] the expansion coefficient of a metal changes with stress. This change is reversible until the applied stress exceeds the elastic limit when there is a discontinuous change in the coefficient. A plastic strain of the order of 2×10^{-6} is said to be sufficient to cause this discontinuity. The same effect appears under cyclic stressing and it is suggested that if the fatigue limit is exceeded this can be indicated by a permanent change in the expansion coefficient. The authors say that incipient damage to large complicated parts might be determined non-destructively by measuring the change in expansion coefficient with strain gauges. This work does not appear to have received any confirmation and, in view of what is known of the distribution of fatigue regions within a metal, it seems unlikely that the measurement of an expansion coefficient over a fairly large volume of the metal would give a sufficiently sensitive indication of any changes that might occur in the affected regions.

ELECTRIC AND MAGNETIC LOSSES

Cavanagh[9] refers to variation in the core loss of a coil carrying high frequency current and surrounding metal undergoing fatigue. Under cyclic stresses below the limit the core loss remains constant, but shows a progressive change when fatigue is occurring. Here, again, these observations do

not seem to have been repeated or applied in any practical manner. However, it is conceivable that in certain materials the electrical conductivity in regions where the fatigue process is in action might be changed appreciably. For example, the electrical conductivity of a precipitation hardening aluminium alloy may vary over the range 2 : 1 according to its metallurgical condition. Since it is known that in certain precipitation hardening alloys the fatigue process may be accompanied by local precipitation which will affect the conductivity, it is possible that if a means for measuring conductivity over a sufficiently limited volume of the metal could be devised a test method could be established for locating the fatigue sensitive areas in alloys of this type.

ULTRASONIC ATTENUATION

Recent work by Truell[10] and others suggests that there is a relation between amount of deformation and ultrasonic velocity and attenuation at high frequencies, and in one reference[11] Truell has indicated that ultrasonic attenuation might relate to the detection of fatigue. It is felt that at present this is more in the nature of a hope than an actual promise, for the same difficulties, which are always encountered, will apply here, namely the application of the method not to specially prepared materials, but to actual working components.

SURFACE EXAMINATION

The Aluminium Company of America[12] have recently referred to a technique of examining chemically polished specimens during fatigue by obtaining, at intervals, plastic replicas of the surface and it is claimed that all stages of fatigue deformation are observable with the replica technique from the innocuous stages involving slip to the more insidious stages involving cracking. This is attractive in its simplicity and in its applicability to components of various shapes. However, the necessity for chemical polishing of the surface may restrict its application as a practical non-destructive test of a component.

Thus, we are forced to the conclusion that, at present with the techniques available, there is no non-destructive test that can be applied to the detection of fatigue in structural components before the formation of an actual crack in the material.

DETECTION OF CRACKS

Some practical attempts have been made to detect the formation of a crack during the service of components subject to fatigue stresses. As a means of forestalling fatigue failure these methods are somewhat hazardous since the amount of the total life that remains after the first formation of a small crack is a very variable quantity. In an appendix to a paper by McGuigan and others[13] a method is described of detecting fatigue cracks through the use of fine copper wires bonded to the surface in the region where fatigue cracks are expected to appear, the formation of a crack causing the wire to rupture and break the passage of an electric current. This method appears to be applicable when it is known that a fatigue crack is likely to occur in a certain region. Similarly it is possible to locate a small coil carrying high frequency current on the surface of a component in a vicinity where a crack is expected to form. Formation of a crack interrupts the induced current loop in the metal and causes a corresponding change in the electrical constants of the coil. By these means it has been possible to show experimentally that cracks approximately 1 mm long and 0·5 mm in depth may be detected (Fig. 3).

As fatigue cracks are almost always open to the surface of the material the conventional methods of crack detection, such as the penetrant or magnetic methods may be applied when the crack has grown sufficiently and are, in fact, the basis of most methods of intermittent inspection for detecting

Fig. 3. Fatigue cracks the formation of which in transverse bending was detected by the change in impedance of a pancake coil attached to the surface of the metal. The coil had 600 turns 46 s.w.g. enamelled copper wire and had the dimensions 15/32 in. O/D; 5/32 in. I/D; 1/16 in. thickness, and formed part of a bridge circuit carrying 10 kc/s alternating current (×5)

fatigue damage. The drawbacks are that inspection is intermittent and is sometimes difficult to apply because of the inaccessibility of components likely to suffer fatigue damage. In certain cases ultrasonic and radiographic inspection are also applicable.

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Structural changes and energy dissipation during fatigue in copper

By N. Thompson, Ph.D., F.Inst.P., and N. J. Wadsworth, B.Sc., Ph.D., H. H. Wills Physics Laboratory, University of Bristol

Simultaneous observations have been made of the metallographic changes visible on the surface, and of the changes in energy dissipation, which take place during the fatigue testing of specimens of fully annealed copper. The apparatus and methods used are briefly described, and the results summarized. It is maintained that, in this case at least, there is no direct connexion between the changes in energy dissipation and the progress towards fatigue failure, and other experiments in support of this thesis are described.

INTRODUCTION

When a solid is subjected to a repeated cycle of stress, as in a fatigue test, the graph of stress against strain is frequently not single-valued, but is a closed loop. The area of this loop is equal to the energy dissipated per unit volume per cycle. Many observations have been made of this quantity, and of its variations with stress, and with repeated application of constant stress. It has frequently been suggested that observations of this kind might be relevant to problems relating to the eventual fracture of the material.

During the course of some recent experiments on the fatigue of copper, which were mainly concerned with metallographic matters, observations were also made from which it is possible to deduce the changes which occurred in the energy dissipation during the fatigue test. The purpose of this paper is to present these results, to examine the correlation with the metallographic observations and to consider to what extent measurements of energy dissipation may in general be expected to be relevant to fatigue fracture.

APPARATUS

The machine used is shown diagrammatically in Fig. 1. It is designed to produce an axial alternating tensile-compressive (push-pull) stress on a cylindrical specimen. The specimen S is supported at the top by the massive framework of the machine. The work coil C is attached to the bottom of the specimen and moves in the gap G of a large permanent magnet PM. When an alternating current is passed through the coil an alternating force is produced. It is arranged that the frequency of alternation coincides with the resonant frequency determined by the mass of the coil former M oscillating on the specimen S as a spring (about 1000 c/s). Since the machine is radially symmetrical and the coil former is unconstrained, a good degree of axiality of loading is achieved. At resonance, the amplitude of the force variations in the specimen is Q times that produced by the coil. (Q is defined, by analogy with electrical resonant circuits, as 2π (stored energy)/energy dissipated per cycle.) The force on the specimen is measured by a piezoelectric force meter SM at the top of the specimen, and the force exerted by the coil is proportional to the current through it. Thus the Q of the resonant system is measured, after suitable calibration, by the ratio of the force on the specimen to the coil current. The machine was not specifically designed to measure the energy dissipated in the specimen but it is possible to do this, at least approximately. The most direct method is to measure the rate of heat evolution in the specimen itself. This can be done by affixing a thermocouple and observing the initial rate of rise of temperature on first starting the machine. An alternative method which gives continuous readings throughout a fatigue test is to measure the Q of the resonant system as a whole. The energy dissipated is proportional to $1/Q$ and it was found that the contribution to $1/Q$ from the rest of the machine—apart from the gauge length of the specimen—was independent of stress. Thus the $1/Q$ of the specimen itself can be obtained, at least approximately, by subtracting a constant from the value found from the ratio of the force on the specimen to the coil current. The constant to be subtracted must be determined afresh each time a new specimen is put in the machine, but may be taken as being equal to the whole $1/Q$ at low stresses. Obviously this method is only of use for specimens with considerable energy loss, e.g. annealed specimens of pure metals. It is useless for materials like Dural with low losses, as these are masked by the machine losses, but as it allows measurements to be taken continuously during the test it was used in all the work to be described. A number of cross-checks showed that the two methods gave consistent results.

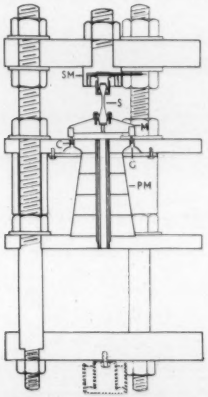

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Fig. 1. Diagram of fatigue machine

MATERIALS

In all the tests to be discussed annealed specimens of pure metals were used in an attempt to simplify the problem as far as possible. Most of the work was done on oxygen-free high conductivity copper although some work on nickel, aluminium and cadmium will be mentioned.

DEVELOPMENT OF FATIGUE CRACKS

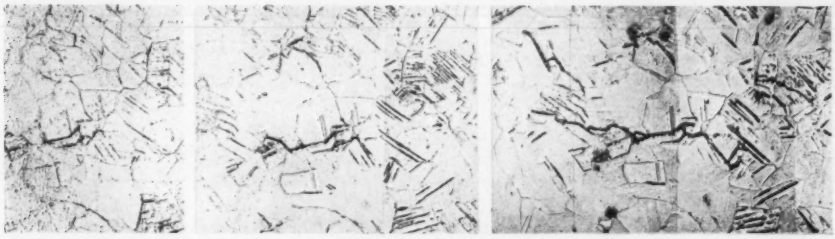
Measurements were made of the energy dissipation at all stages of the fatigue tests. The surfaces of the specimens

were also examined with the aid of a microscope at intervals during the tests. The results of the metallographic examination of the copper specimens have already been fully described elsewhere (Thompson, Wadsworth and Louat[1]). The results may be summarized very briefly as follows:

Very early in the test slip bands appeared on the specimen. These became more numerous, and in general more intense as the test proceeded, and finally fatigue cracks formed in some of them. It was not possible to see when the cracks first formed. However, if the specimen were lightly electropolished at intervals, the slip bands were removed, and the formation of cracks could be more easily detected. It was found that by about 5% of the life of the specimen some slip bands became "persistent," that is to say, they were attacked by the electropolish which removed the others. As the test proceeded the number and length of these persistent marks increased. After about 45% of the life the first one started to spread to the next grain. (The grains were about 0·1 mm in diameter.) At this stage it was undoubtedly a crack, and opened up if the specimen were stretched. The remaining 55% of the life was occupied by the spreading of the crack. Figs. 2(*a*) to 2(*c*) show various stages in this progress.

The above refers to polycrystalline copper. The process of crack formation was very similar in single crystals of copper. In the case of nickel, tested at stresses which gave a life of a few million cycles, the number of slip bands produced was very much less, and most of the surface of the specimen remained free from markings throughout. But even here, some few persistent slip bands could be detected after about 5% of the life, and it was from these that the cracks ultimately grew.

Similar observations have been made on aluminium and aluminium alloys by Smith and Harries[2] and this work has led to similar conclusions. The principal difference is that, in aluminium at room temperature, the cracks appear to form more often in grain boundaries than in slip planes; at lower temperatures, however, the behaviour is more nearly akin to that of copper at room temperature. The only other material upon which any number of observations have been made is cadmium, in the form of single crystals. Here the behaviour was quite different. It happened that the specimens tested were oriented with the hexad axis approximately normal to the tensile axis. This is an unfavourable orientation for deformation by slip but is favourable for twinning under the action of a tensile stress. Such twins were in fact formed and, once formed, rapidly became more numerous as the test proceeded. The boundary between twin and matrix, although of normal appearance when the twin first appeared, soon became marked by rather irregular black lines (Fig. 3). It was along a section of one of these boundaries that the fatigue crack formed.



(*a*) (*b*) (*c*)

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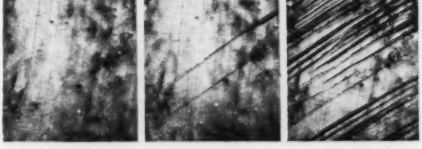
Fig. 2. Stages in the growth of a fatigue crack in copper

(*a*) electropolished after 5½% of life (*b*) electropolished after 44% of life
(*c*) electropolished after 71% of life



(*a*) (*b*) (*c*)

Fig. 3. Stages in the proliferation of twin bands in a single crystal of cadmium during fatigue

ENERGY LOSS MEASUREMENTS

The variations in energy dissipation can conveniently be described during two periods: firstly the initial hardening on first stressing the specimen, and secondly the subsequent changes during a fatigue test.

When a fully annealed copper specimen was first tested it was very soft, i.e. the energy dissipation was large. On first switching on the machine, it took perhaps a thousand cycles (i.e. a second) for the oscillations to build up and become stable at the operating stress. This represented the earliest point at which significant observations could be made. From this point onwards the energy loss fell rapidly for about 10^4 cycles, and then continued to fall at a decreasing rate, provided that the stress was very low. If the copper were less thoroughly annealed (e.g. 1 h at 400° C instead of 500° C) this initial rapid drop was completely absent. A similar initial rapid fall was observed on the one or two aluminium specimens tested and on numerous nickel specimens. A single crystal of cadmium showed the same general behaviour but over a much extended time-scale (about ×100). It is not proposed to discuss this initial hardening phase in this paper.

Turning now to the second period, and again referring in the main to results on copper, it was found that if the stress were sufficiently high, then, after the initial rapid fall, the energy loss began to rise again, and continued to increase for the rest of the test. Fig. 4 shows a typical example. If, as mentioned in a previous paragraph, the material is not fully

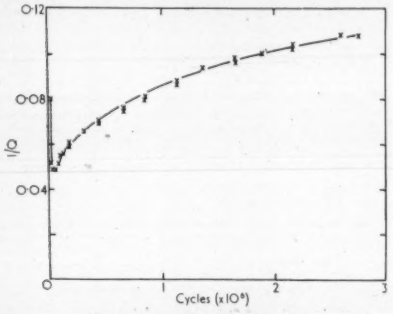


Fig. 4. Variation of energy dissipation ($1/Q$) during a fatigue test on annealed copper

annealed so that the initial rapid decrease in $1/Q$ is not observed, the curve of $1/Q$ against number of cycles rises monotonically from the beginning. The highest value of energy loss, just prior to fracture, was always of the same order of magnitude, but showed so much random variation that it could not be called a constant. On the other hand, the initial* rate of increase of $1/Q$ varied over a very wide range. A change of 15% in stress caused a change in this initial rate of rise by a factor of order 100. This is illustrated in Fig. 5, which shows a set of curves for twelve specimens tested at stresses ranging from $1{\cdot}03 \times 10^9$ to $1{\cdot}20 \times 10^9$ dyn/cm^2. (Note the variations in the horizontal scales.) The change in fatigue life due to such a change in stress is of the same order. Indeed, there is a good correlation between the rate of rise of $1/Q$, and the fatigue life, provided all factors other than the stress are held constant. This is shown by Fig. 6 in which the two quantities are plotted one against the other. The two sets of points refer to two groups of specimens which had received different annealing treatments. It looks at first sight as if this correlation might afford a good method of predicting fatigue life; but further experiments, to be mentioned below, show that this is not true in any useful sense.

During the course of a fatigue test the number of slip bands on the surface of a specimen increases. On one specimen an attempt was made to obtain some quantitative measure of this increase. The same region of the specimen was photographed at intervals during the test, and a count made of the number of lines visible in a certain area. Such a procedure is necessarily very approximate, but if the number of lines is plotted against $1/Q$, as the two quantities increase during the test, the points lie near to a straight line. If, further, we remember that there is a constant to be subtracted from all observed values of $1/Q$, to take account of machine losses, we can conclude that the relation is, approximately, one of proportionality.

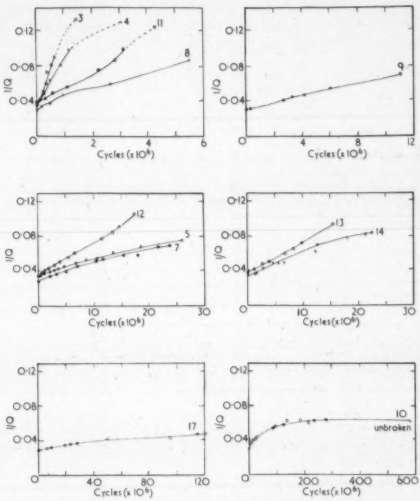


Fig. 5. Variation of energy dissipation during fatigue of copper: twelve specimens at different stresses. (Note different time scales.) The number against each curve refers to the corresponding point in Fig. 6

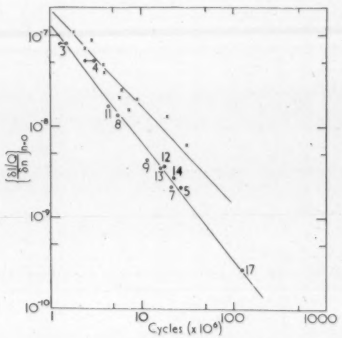


Fig. 6. Initial rate of rise of energy loss correlated with fatigue life

○ standard preparation.
× standard preparation, 500° C anneal.

The above account all refers to observations on copper. When similar experiments were done on nickel, the results were quite different. It has already been mentioned that very

* With fully annealed specimens, the rapid fall of $1/Q$ mentioned in the previous paragraph was ignored when calculating the "initial" rate of increase in the present context.

few slip bands were to be seen on such specimens at the conclusion of the test, except for those in the immediate neighbourhood of the crack, which had clearly arisen owing to the large stress concentrations near the advancing tip. The corresponding measurements of energy loss showed that, after the initial rapid drop, $1/Q$ remained sensibly constant throughout the test until very shortly before the final failure. Two specimens which were tested at higher stresses, and gave fatigue lives of the order of $0{\cdot}5 \times 10^6$ cycles, provided exceptions: in these cases the graph of $1/Q$ began to rise after about 75% of the life had expired. To correlate with this observation, it may be noted that the surfaces of the fractured specimens showed a much more widespread distribution of slip markings than usual.

The few aluminium polycrystals tested showed a continuous increase in $1/Q$ during the fatigue test, and a continuous increase in the number of visible slip bands. This behaviour is closely similar to that of copper, but no quantitative results are available.

The observations on cadmium single crystals are of interest. It has already been mentioned that the initial high energy loss decreased only slowly. At low stresses this was all that happened. But at higher stresses, some time during this decrease there would suddenly be a clicking noise from the specimen and the energy loss would simultaneously increase. If the machine were stopped quickly, and the specimen examined, it would be found that a band of twins had formed on the crystal. On continuing the test at the same stress the energy loss would increase very rapidly, accompanied by further clicks and the appearance of increasing amounts of twinning. Failure, along a twin-matrix interface, followed very rapidly (see Fig. 3).

Three other experiments should be mentioned, all dealing with the relation between energy dissipation measurements and fatigue life:

(1) If a specimen were taken from the fatigue machine part-way through a test, and annealed, most of the increase that had occurred in $1/Q$ was removed, but the fatigue life was not appreciably affected. Fig. 7 shows a graph of $1/Q$ against a number of cycles for a specimen which was annealed in this way after every 20% of its normal life. The annealing was done *in vacuo* for one hour at 600° C and was followed by a slow cooling. After each anneal the initial energy loss was very high, but dropped rapidly to a low value, as at the beginning of the test. No measurements of this initial drop were made, but the results are indicated diagrammatically in Fig. 7. This specimen eventually broke after a time appropriate to an uninterrupted test. One or two other specimens tested in the same way gave similar curves, and also showed that the intermediate annealing had no marked effect on the fatigue life. The same result was obtained by Sinclair and Dolan[3] who annealed brass specimens above the recrystallization temperature either every 50% or every 20% of their expected lives. The fatigue life of these specimens was statistically indistinguishable from that of a control group tested without interruption. Similarly Smith and Harries[2] did intermediate annealing experiments on aluminium specimens (30 min at 350° C) and again found no statistically significant effect on the life. Yet another example is provided by the work of Laute and Sachs[4] on nickel; these observations were not so extensive as the previous two sets but led to the same conclusion.

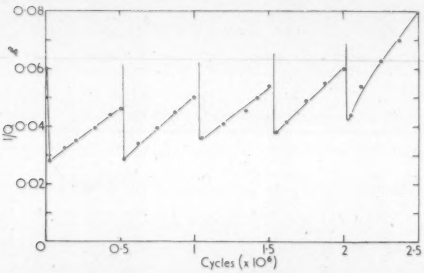


Fig. 7. Variation of energy dissipation during fatigue of annealed copper: test interrupted four times, and specimen annealed 1 h at 600° C

(2) If the specimens were heavily electropolished at intervals, to a depth sufficient to remove the traces of the persistent slip bands, the fatigue life could be increased. The value of $1/Q$ was, however, unaffected by this treatment, as far as could be judged in view of the change of zero when the specimen was removed from, and replaced in, the machine.

(3) Specimens tested in an atmosphere of oxygen-free nitrogen, instead of laboratory air, gave a fatigue life greater than normal by a factor of about 5 (see table). This is in agreement with the earlier results of Gough and Sopwith.[5]

Relation between fatigue life of specimens tested in air and nitrogen

Specimen No.	*Atmosphere*	*Life* (× 10^6 *cycles*)
58	Air	3·3
66	Nitrogen	20·3
67	Air	3·4
68	Nitrogen	10·4
69	Air	3·2
70	Nitrogen	17·5

On the other hand, the early rate of increase of $1/Q$ was not significantly different from the two groups of specimens.

DISCUSSION

The previous results can be summarized as follows: The energy dissipation in the specimen, its $1/Q$, and also its fatigue life are both connected with the formation of broad slip bands. The energy loss is considerably affected by annealing a partially fatigued specimen. But on the other hand it is not affected by the removal of surface layers of metal or by changes in the surrounding atmosphere. It is, in fact, a bulk phenomenon, depending on changes taking place throughout the volume.

The formation and/or propagation of fatigue cracks, however, can be affected by changes in the atmosphere; and the development of the final fatigue failure can be inhibited by the removal of the surface. Thus fatigue failure is primarily a surface phenomenon.

Since the two effects are both connected with processes taking place in slip bands, it is perhaps not surprising that a correlation exists between the two if all other factors except the level of applied stress are kept constant. But it is equally clear that there is ample scope for such other factors to affect the two phenomena quite differently. There is no reason, for example, to expect that alloying, or heat treatment, or cold working or specimen shape will affect the two

phenomena in the same way; and thus such correlation as does exist is of little practical value.

It is perhaps worth pointing out that the experiments which have been described have been done under conditions in which the stress was (macroscopically) almost uniform throughout the gauge length. Such conditions are particularly favourable for evaluating the significance of changes in energy loss. With other modes of stressing (e.g. reverse bend and torsion) all stresses from zero up to a maximum are present. Now the energy dissipation per unit volume is a rapidly increasing function of the stress, so that the observed energy loss will be some kind of weighted mean of all values up to the maximum. Moreover the weighting function itself will vary with stress, and with time during the course of one test. But the arguments advanced above to suggest that a general correlation between energy loss and fatigue should not be expected, are equally valid for these conditions.

There is another reason for doubting the usefulness of energy loss measurements as a diagnostic for fatigue. Apart from the initial rapid drop, which we do not propose to discuss further, the experiments described suggest that the rate of energy dissipation is closely related to the total number of active slip bands. This view received a direct confirmation from an experiment made on a copper specimen at a very low stress. After $0{\cdot}2 \times 10^6$ cycles, the energy loss was very small, and practically no slip bands were visible. The test was then continued for about 100×10^6 cycles, the energy loss and number of slip bands rising slowly all the time. At this point the specimen was electropolished, and almost all the slip bands were removed. On fatiguing for a further $0{\cdot}2 \times 10^6$ cycles at the same stress, however (the value of the energy loss remaining at the same comparatively high level), a large number of slip bands had again become visible.

The observations on the cadmium crystals are in line with this viewpoint, if we recall the dislocation mechanisms involved. In a slip band, whatever may be the details, there will be a large number of dislocations moving to and fro under the action of the alternating stress. Similarly if, as appears probable, the twin-matrix interface moves to and fro under similar conditions, this will be brought about by the movement of numerous twinning dislocations along the interface. If the former gives rise to a dissipation of energy, so also will the latter.

On the other hand, of all the slip bands, only a few of those visible on the surface (themselves only a few of the total number) show any tendency to develop into a crack, and in only a few of these does the development proceed very far. Thus while the energy loss measurements give a numerical measure of some quantity averaged over all slip bands, the fatigue crack starts from one of a few bands which are, in some way as yet unknown, exceptional. It is natural, but probably not essential, to postulate that the development of microcracks has already begun very early in the test. In this way we can obtain a simple explanation of the results of the annealing experiments which restore the crystal in and near the slip bands to something approaching its virgin condition, but do not appreciably heal any incipient cracks already forming on the surface.

Finally, we may note that all the observations described have been made on nominally pure and stable metals. Similar experiments on more complex substances are likely to give more complex results. Many alloys of technical interest appear to derive their desirable properties from the fact that, under normal conditions of service, they are only in metastable equilibrium: precipitation hardening systems are an obvious example. There is a good deal of evidence that, under fatigue conditions, precipitation can proceed at an increased rate, and takes place preferentially in the slip bands. Thus the act of carrying out a fatigue test is itself producing metallurgical changes in the material being investigated. If this, and other similar effects, are at all general, then there does not seem to be much hope for a satisfactory accelerated fatigue test, which would reduce the time involved in routine testing.

Commenting on the above paper, **Dr. R. F. Hanstock** (High Duty Alloys Ltd.) said: I would like to compliment Dr. Thompson on the elegance of the photographs showing the development of fatigue cracks in copper and to make the following comments on the measurement of damping capacity. The negligible effect observed on annealing after cyclic stressing suggests that a crack may have been developed before annealing and it would be interesting to know the extent to which the increase observed in the damping of copper during cyclic stressing is attributable to crack formation and growth.

The relative insensitivity of the change in damping during cyclic stressing is probably due, as suggested by Dr. Thompson, to the fact that the damping measured is the average damping of the whole specimen stressed uniformly under direct stress. Greater sensitivity to change in surface properties may be obtained for those modes of stressing which give a maximum stress at the surface, e.g. the bending or torsion modes.

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Measurement of elastic constants by the ultrasonic pulse method

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Definitions of stress and strain are given in terms of force and differential coefficients of displacement respectively and the generalized form of Hooke's law stated. This defines the elastic constants of a general aeolotropic medium. Special cases of cubic and hexagonal symmetry are considered. The elastic wave equations are derived for plane waves in an infinite aeolotropic solid. The velocities of the three types of wave are given for certain directions in cubic and hexagonal materials. Difficulties may be encountered in propagation of waves along axes other than principal ones due to the oblique path along which the energy travels. This may limit the use of the method to certain directions depending upon the geometry of the specimen. A brief outline of the apparatus used is given and the accuracy which may be achieved is discussed. The method may be applied to polycrystalline materials provided that the grain size is reasonably small.

INTRODUCTION

Most engineers or structural architects are usually only concerned with isotropic materials. The elastic properties of these materials may be defined by only two constants, for example, Young's modulus and rigidity modulus. The metal physicist is, however, more interested in the forces of attraction or repulsion in a crystal lattice and the measurement of elastic constants of such a lattice is a very useful tool for investigating these inter-atomic forces. Usually a lattice will not behave in an isotropic fashion as far as the elastic properties are concerned, and if there is no symmetry in the system there will exist as many as twenty-one independent elastic constants.

In the past, elastic constants of single crystals were usually measured by a static method and information in the literature on their values was in many cases lacking and sometimes inconsistent. This was due largely to the fact that attempts to measure very small displacements on single crystals usually very limited in size, led to difficulties in maintaining a high standard of sensitivity. Furthermore, the elastic range of single crystals is usually such that the applied stress must be kept low in order that Hooke's law may be obeyed.

Many of the difficulties encountered in static testing are obviated by the ultrasonic pulse method. The applied stress is negligibly small and a high sensitivity is attained on small specimens. The method is easy to apply and the only requirement of the specimens is that they should have pairs of flat surfaces parallel to each other and normal to known crystallographic directions.

The elastic constants are deduced from measurements of wave velocities in given directions. The only other factor which is required to be known is the density of the material.

It is shown that in materials which are elastically aeolotropic, there are three types of plane wave motion possible in any given direction. In one mode the particle motion of the vibrations is nearly longitudinal and in the remaining two nearly transverse with respect to the wave front. For materials which are isotropic only two types of plane wave motion are possible and these are truly longitudinal or transverse.

DEFINITION OF ELASTIC CONSTANTS

When a body is distorted from its normal shape by the application of external forces, the body is said to be strained. The physical effect of this which is most apparent is that points on the body have taken up new positions relative to the old. For example, when external forces are applied to the rectangular lamina shown in Fig. 1, the relative points $A\,B\,C\,D$ move to $A'\,B'\,C'\,D'$. The body is said to be in a state of both longitudinal and shear strain.

In a three dimensional body, suppose that the displacement of any point in the x, y, z directions is u, v, w. Assuming the displacements are small (i.e. using only the first term of the

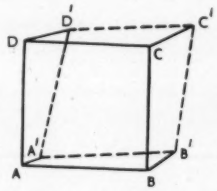

Fig. 1. Distortion of rectangle $ABCD$ to A', B', C', D' resulting from application of external forces

Taylor expansion) compared with the dimensions of the body, the total strain at any point may be expressed by six components, three longitudinal and three shear.

They are:

$$\left.\begin{aligned} e_{xx} &= \frac{\partial u}{\partial x} \\ e_{yy} &= \frac{\partial v}{\partial y} \\ e_{zz} &= \frac{\partial w}{\partial z} \\ e_{yz} &= \frac{\partial w}{\partial y} + \frac{\partial v}{\partial z} \\ e_{zx} &= \frac{\partial u}{\partial z} + \frac{\partial w}{\partial x} \\ e_{xy} &= \frac{\partial v}{\partial x} + \frac{\partial u}{\partial y} \end{aligned}\right\} \qquad (1)$$

The physical change which is most readily appreciated, namely displacement, has now been replaced by differential coefficients of displacement to define completely the six components of strain at any point.

Generalized Hooke's law. The stress applied to a body may also be defined by six components. Three of these are normal stress applied to the x, y and z planes and designated

$\widehat{xx}$, $\widehat{yy}$, $\widehat{zz}$ respectively and three are shear stresses in the x, y, z planes and designated by $\widehat{yz}$, $\widehat{zx}$, $\widehat{xy}$ respectively. It follows from the conditions of equilibrium of the body that $\widehat{yz} = \widehat{zy}$, etc.

Hooke's law in its most generalized form relates these six components of stress to the six components of strain by six equations of the following type:

$$\widehat{xx} = c_{11}e_{xx} + c_{12}e_{yy} + c_{13}e_{zz} + c_{14}e_{yz} + c_{15}e_{zx} + c_{16}e_{xy} \quad (2)$$

or in tensor notation:

$$f_r = C_{rs}e_s,$$

where $f_1 = \widehat{xx}$, $e_1 = e_{xx}$ and two similar relations, and $f_4 = \widehat{yz}$, $e_4 = e_{yz}$ and two similar relations.

In order that the strain energy of deformation is completely recoverable in removal of stress (i.e. that the process of elastic deformation is reversible) it is necessary that $C_{rs} = C_{sr}$. It therefore follows that the total number of elastic constants required to define the elastic behaviour of the general aeolotropic medium is twenty-one.

If we consider these twenty-one elastic constants, we see that they fall into definite groups. Writing them as:

$$\begin{array}{cccccc} c_{11} & c_{12} & c_{13} & c_{14} & c_{15} & c_{16} \\ & c_{22} & c_{23} & c_{24} & c_{25} & c_{26} \\ & & c_{33} & c_{34} & c_{35} & c_{36} \\ & & & c_{44} & c_{45} & c_{46} \\ & & & & c_{55} & c_{56} \\ & & & & & c_{66} \end{array}$$

c_{11}, c_{22}, c_{33} relate the longitudinal strains to the longitudinal stresses.

c_{44}, c_{55}, c_{66} relate the shear strains to the shear stresses. c_{23}, c_{31} and c_{12} relate the lateral contractions to the longitudinal extension when the material is under uniaxial tension. In fact uniaxial tension f is composed of hydrostatic stress equal to $\frac{1}{3}f$ and two shear stresses, each equal to $\frac{1}{3}f$. In the case of cubic symmetry, the total strain is made up by a bulk strain inversely proportional to $(c_{11} + 2c_{12})$ and two shear strains inversely proportional to $(c_{11} - c_{12})$. The latter difference should therefore be regarded as a shear constant on an equal footing with c_{44}.

Any crystal—even one having cubic symmetry—when referred to axes other than axes of symmetry, has all twenty-one effective constants different from zero. However, when referred to the principal axes of symmetry, interaction between shears and direct strains and between shears in different planes occurs only when the symmetry is low.

The constants c_{56}, c_{46} and c_{45} relate shear strains in one direction to shear strains in another, and the group of nine $c_{14} \ldots c_{36}$ are basically similar. However, in low orders of symmetry [such as monoclinic (13 constants) and triclinic (21 constants)], hydrostatic stress may itself cause shear strain and the corresponding factors of proportionality are also comprised in this group.

Symmetry of crystals. Crystals fall into different classes according to their symmetry[1] and hence the number of independent elastic constants required to define their elastic properties varies. Most metals, however, fall into the cubic class with a few in the hexagonal, tetragonal and trigonal classes.

Metals such as aluminium, copper (face-centred cubic) and iron (body-centred cubic) have cubic lattices and because of their symmetry only three independent elastic constants are necessary. Zinc has hexagonal symmetry and has five independent constants. Antimony and bismuth have a form of trigonal symmetry resulting in six independent constants.

For cubic symmetry, the following relations exist:

$$\begin{aligned} c_{11} &= c_{22} = c_{33} \\ c_{12} &= c_{23} = c_{13} \\ c_{44} &= c_{55} = c_{66} \end{aligned}$$

All other constants are zero.

For hexagonal symmetry, the stress-strain equations are:—

$$\begin{aligned} \widehat{xx} &= c_{11}e_{xx} + c_{12}e_{yy} + c_{13}e_{zz} \\ \widehat{yy} &= c_{12}e_{xx} + c_{11}e_{yy} + c_{13}e_{zz} \\ \widehat{zz} &= c_{13}e_{xx} + c_{13}e_{yy} + c_{33}e_{zz} \\ \widehat{yz} &= c_{44}e_{yz} \\ \widehat{zx} &= c_{44}e_{zx} \\ \widehat{xy} &= \tfrac{1}{2}(c_{11} - c_{12})e_{xy} \end{aligned}$$

It may be seen that this form of symmetry has isotropic properties in the z plane.

PROPAGATION OF PLANE WAVES IN AN AEOLOTROPIC MEDIUM

One method of determining the values of the elastic constants of a material is to measure the velocities at which the three types of plane wave travel in known directions. It will be shown that these velocities are dependent only on the elastic constants, the direction in which the wavefront travels with respect to the crystallographic axes and the density.[2] Assuming that the latter two are known, it is possible to calculate the elastic constants from measurements of the wave velocities.

If (u, v, w) are the components of displacement at any point (x, y, z) we may write Hooke's law in terms of these displacements as follows:—

$$\widehat{xx} = c_{11}\frac{\partial u}{\partial x} + c_{12}\frac{\partial v}{\partial y} + c_{13}\frac{\partial w}{\partial z} + c_{14}\left(\frac{\partial v}{\partial z} + \frac{\partial w}{\partial y}\right) + \\ + c_{15}\left(\frac{\partial w}{\partial x} + \frac{\partial u}{\partial z}\right) + c_{16}\left(\frac{\partial u}{\partial y} + \frac{\partial v}{\partial x}\right) \quad (3)$$

and five similar equations for the other stresses.

The dynamic equations of equilibrium of a small element of the medium are

$$\left.\begin{aligned} \frac{\partial}{\partial x}\widehat{xx} + \frac{\partial}{\partial y}\widehat{xy} + \frac{\partial}{\partial z}\widehat{xz} &= \rho\frac{\partial^2 u}{\partial t^2} \\ \frac{\partial}{\partial x}\widehat{yx} + \frac{\partial}{\partial y}\widehat{yy} + \frac{\partial}{\partial z}\widehat{yz} &= \rho\frac{\partial^2 v}{\partial t^2} \\ \frac{\partial}{\partial x}\widehat{zx} + \frac{\partial}{\partial y}\widehat{zy} + \frac{\partial}{\partial z}\widehat{zz} &= \rho\frac{\partial^2 w}{\partial t^2} \end{aligned}\right\} \quad (4)$$

where ρ = density.

We now consider the solution of equations (3) and (4) for an infinite plane wave periodic in time, the wavefront of which is travelling in any direction (l, m, n) where l, m and n are the direction cosines of the normal to the wavefront with respect to the reference axes.

The equation to this wave is given by,

$$(u, v, w) = (A_x, A_y, A_z)F(lx + my + nz - v_n t) \qquad (5)$$

where A_x, A_y, A_z are constants which determine the amplitude of the wave and v_n is the phase velocity.

By differentiating equations (3) and (5) with respect to the appropriate variables and substituting these differentials into (4), we obtain

$$\left.\begin{aligned} (A - \rho v_n^2)A_x + \alpha\beta A_y + \gamma\alpha A_z &= 0 \\ \alpha\beta A_x + (B - v_n^2)A_y + \beta\gamma A_z &= 0 \\ \gamma\alpha A_x + \beta\gamma A_y + (C - \rho v_n^2)A_z &= 0 \end{aligned}\right\} \qquad (6)$$

where A, B, C, $\beta\gamma$, $\gamma\alpha$, $\alpha\beta$, are functions of the elastic constants and l, m, n. The actual values are given in the Appendix.

The condition which gives non-zero values of A_x, A_y, A_z, is

$$\begin{vmatrix} A - \rho v_n^2, & \alpha\beta & , & \gamma\alpha \\ \alpha\beta & , & B - \rho v_n^2, & \beta\gamma \\ \gamma\alpha & , & \beta\gamma & , & C - \rho v_n^2 \end{vmatrix} = 0 \qquad (7)$$

This is a cubic equation in ρv_n^2 and therefore there are three possible velocities of elastic waves associated with any direction, provided that the roots are real and positive.

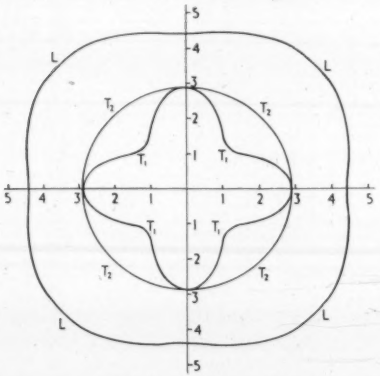

Fig. 2. Velocity in km/s of the three types of wave for any direction in the (100) plane for copper

Furthermore, it can be shown that in general, the particle displacement of the plane wave is neither coincident nor orthogonal to (l, m, n). However, the three types of wave resolve as follows: one in which the particle displacement is nearly longitudinal and two in which it is nearly transverse (e.g. L, T_1 and T_2 in Fig. 2 and 4). In all cases the displacement vectors are at right angles to each other.

The equations simplify very greatly for a medium of cubic symmetry.

Putting $H = \rho v_n^2 - c_{44}$

$a = c_{11} - c_{44}$

$b = c_{12} + c_{44}$

$c = a - b = c_{11} - c_{12} - 2c_{44}$

$\Sigma = m^2n^2 + n^2l^2 + l^2m^2$, $\Pi = l^2m^2n^2$

The cubic equation for the three velocities becomes

$$H^3 - aH^2 + c(a + b)\Sigma H - c^2(a + 2b)\Pi = 0 \qquad (8)$$

Fig. 2 shows the three velocities for any direction in the (100) plane for copper.

PROPAGATION OF ELASTIC WAVES ALONG SPECIAL AXES IN CUBIC CRYSTALS

For reasons that will become apparent later, there are advantages in measuring the velocities of elastic waves along certain directions in single crystals. The velocity equations simplify still further in cubic crystals for the [100] [110] and [111] directions.

For the [100] direction, $l = 1$, $m = 0$, $n = 0$

$\rho v_n^2 = c_{44}$ (transverse)
c_{44} (transverse)
c_{11} (longitudinal)

For the [110] direction, $l = \frac{1}{\sqrt{2}}$, $m = \frac{1}{\sqrt{2}}$, $n = 0$

$\rho v_n^2 = c_{44}$ (transverse)
$\frac{1}{2}(c_{11} - c_{12})$ (transverse)
$\frac{1}{2}(c_{11} + c_{12} + 2c_{44})$ (longitudinal)

For the [111] direction, $l = 1/\sqrt{3}$, $m = 1/\sqrt{3}$, $n = 1/\sqrt{3}$

$\rho v_n^2 = \frac{1}{3}(c_{11} - c_{12} + c_{44})$ (transverse)
$\frac{1}{3}(c_{11} - c_{12} + c_{44})$ (transverse)
$\frac{1}{3}(c_{11} + 2c_{12} + 4c_{44})$ (longitudinal)

The displacement vectors of the waves for these three directions are either in the plane of the wavefront or normal to it, hence the waves are truly transverse or longitudinal. In the [110] direction, the two transverse velocities have extreme values and in the [111] direction, the longitudinal wave travels with maximum or minimum velocity depending on whether $(c_{11} - c_{12} - 2c_{44})$ is positive or negative. In both the [100] and [111] directions the two transverse wave velocities are equal.

MEASUREMENT OF ELASTIC CONSTANTS BY PROPAGATION IN SEVERAL DIRECTIONS WITHOUT KNOWLEDGE OF ORIENTATION

The elastic constants of aeolotropic materials may be deduced from the values of the wave velocities and crystallographic orientation measurements. If, for example, the material is known to have cubic symmetry, the three constants may be calculated from the three wave velocities for one direction only, provided that direction is known in relation to the principal axes, and that the orientation is such that the two transverse wave velocities are not equal. The orientation may be measured by X-ray methods but it is not always possible to do this with sufficient accuracy.

There is, however, an alternative in which the wave velocities are measured in several directions and in certain cases the elastic constants may be deduced without previous knowledge of the orientation of the crystal.

Suppose, for example, a specimen, having cubic symmetry, is machined into a bar with octagonal cross-section and that the three wave velocities are measured in each direction normal to the octagonal faces.

For any direction we have as before

$$H^3 - aH^2 + c(a + b)\Sigma H - c^2(a + 2b)\Pi = 0$$

If *a*, *b*, *c*, *d*, *e* are the directions normal to faces shown in Fig. 3 and we designate to each of these directions the appropriate values of Σ and Π (e.g. for the *a* direction, Σ_a and Π_a), it is indicated in the appendix that for an octagonal configuration, certain relations between the values of Σ and Π exist.

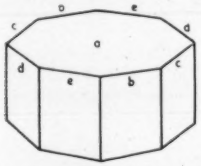

Fig. 3. Single crystal specimen cut with octagonal cross-section for the determination of elastic constants without knowledge of orientation

The elastic constants may be calculated by finding the best fitting values to make the relations between the various directions compatible. After the best fitting set has been found, the orientation of each face may be deduced.

DIFFICULTIES ENCOUNTERED IN THE ABOVE METHOD FOR DETERMINATION OF ELASTIC CONSTANTS

This method would appear to be quite an attractive one since no previous knowledge of the orientation is required. Furthermore, the equations derived are self checking and the orientation of the specimen may finally be calculated. It was used with moderate success on a copper crystal with orientations of each face not differing greatly from [100] or [110]. Other crystals of copper and silver were similarly machined in octagonal form and when an attempt was made to measure the three wave velocities along normals to each of the faces, it was found in some cases impossible to receive all three modes of propagation. This effect was explained when Musgrave[3,4] showed that the energy of an elastic wave in an aeolotropic medium will not, in general, travel along the same path as the normal to the plane wavefront but can deviate as much as 45° from this.

Furthermore, there is to be considered the practical difficulty of machining the single crystal into octagonal form with great precision and without damaging the material, causing distortions of the lattice.

OBLIQUE PROPAGATION OF ELASTIC WAVES IN AN AEOLOTROPIC MEDIUM

We have seen in the section on the propagation of plane waves that the three types of elastic waves each travel with different velocities in an aeolotropic material according to the direction in which they are propagated. The three wave velocities may be represented by a surface of three sheets, the shape of which depends on the values of the elastic constants for the material. In the isotropic case, this velocity surface degenerates into two concentric spheres representing the longitudinal and shear velocities.

This velocity surface, it will be remembered, represents the velocity of infinite plane waves and it therefore follows that all points on any plane will vibrate with the same amplitude at the same time. This state clearly cannot be attained in practice since the size of the specimen and the transducers used to excite the waves is necessarily finite.

In order to determine the direction of maximum energy propagated from a source of finite size, it is necessary to construct the wave surface as distinct from the velocity surface. A full treatment is given by Musgrave[3] and particular examples of wave surfaces have been calculated for some hexagonal and cubic materials.[3,4]

The wave surface is the surface on which all points will vibrate in the same phase at $t = 1$ when a point source of disturbance is discharged at the origin at $t = 0$. If Huygen's construction is made from a wave surface, the position of maximum energy in the plane of the wave may be found.

Fig. 4 shows the intersection of the wave surface for copper with the [100] plane corresponding to the velocity surface

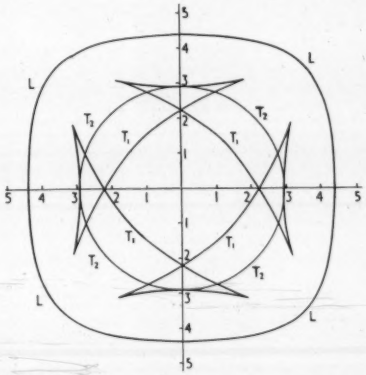

Fig. 4. Intersection of wave surface with the (100) plane for copper

(*Scale:* Distance in km after an elapse of 1 s from the origin of the disturbance.)

shown in Fig. 2. It will be seen that the shape is entirely changed and due to the greatly aeolotropic properties of copper, the wave surfaces are far from spherical.

Fig. 5 shows a typical longitudinal wave surface for a zinc crystal (hexagonal) projected on the *yz* plane. Due to the elastic properties of hexagonal materials, the wave surface has a circular section in the *xy* plane but not in the *yz* plane. If a quasi-longitudinal wave is propagated along a direction *ON* which is inclined at 15° to the *z* axis, the position of maximum energy, which is given by the Huygen's construction, is at *L* which is the point of contact with the plane normal to *ON* and the wave surface. It will be seen that the deviation of the energy path *OL* from *ON* is considerable. (The diagram is drawn approximately to scale.) It must be borne in mind that the wave travels with a phase velocity (V_l) associated with the *ON* direction and not *OL* in spite of the fact that the energy has travelled along an oblique path.

Fig. 6 is a demonstration of a zinc crystal through which longitudinal waves are propagated. Quartz crystals T_x and R_x

are attached to opposite faces of the zinc and it is found that no energy is received at *A* from a pulse transmitted from *C* (i.e. when the quartz crystals are directly opposite each other), but maximum energy is received when the upper crystal is moved to *B*.

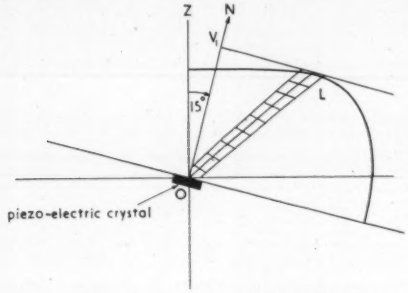

Fig. 5. Partial section of longitudinal sheet of wave surface for zinc showing deviation of rays from wave normal

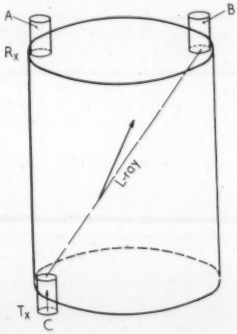

Fig. 6. Oblique propagation of quasi-longitudinal waves in zinc crystal with the wave normal inclined 15° to *z*-axis
A, no energy received here; *B*, maximum energy received here.

For an example of propagation in an arbitrary direction, details of a measurement of elastic constants for pure iron are given. The test was made on the broken end of an impact test piece and for which reason the results may be in doubt. The specimen contained several large crystals which could not readily be separated. However, one extended across the entire width of the bar, and the orientation of the faces of this crystal was found by the X-ray back reflexion method (Fig. 7).

The three wave velocities were measured and the results were as follows:—

Orientation with respect to	⟨100⟩	⟨010⟩	⟨001⟩
	13°	77°	87°

Wave velocities $5{\cdot}663 \times 10^5$ cm/sec (quasi-longitudinal)
$3{\cdot}832 \times 10^5$ cm/sec (transverse)
$3{\cdot}520 \times 10^5$ cm/sec (quasi-transverse)

The elastic constants were determined using equation (8) and were:

$$c_{11} = 23{\cdot}30 \times 10^{11}\ \text{dyn/cm}^2$$
$$c_{12} = 13{\cdot}92 \times 10^{11}\ \text{dyn/cm}^2$$
$$c_{44} = 11{\cdot}62 \times 10^{11}\ \text{dyn/cm}^2$$

assuming $\rho = 7{\cdot}870$.

From diagrams prepared by Mr. M. J. P. Musgrave, the angle between the wave normal and the ray or path of energy was estimated to be about 10° towards [110] for the longitudinal wave and 30° towards [1$\bar{1}$0] for the slower transverse wave; within the limits of estimation, the deviation of the fast transverse wave was zero.

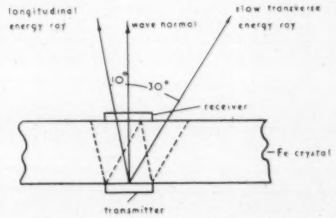

Fig. 7. Propagation in crystal of iron

The amplitudes of the received pulses bore some witness to the correctness of these estimates, since the amplitude of the slower transverse wave was significantly lower than the amplitude of the faster. This may well have been due to a substantial proportion of the energy of the slower wave reaching the receiving face outside the area of contact of the receiving transducer which in fact was mounted directly opposite the transmitter. Thus for a path length of $\frac{3}{8}$ in. and deviation of 30°, the displacement of the centre of the energy beam is $\frac{3}{8}\tan 30° = 0{\cdot}22$ in. which is just less than the diameter of the transducers used.

Again it must be pointed out that this oblique propagation of energy is associated with a phase velocity corresponding with the wave normal defined by the parallel faces and it is this quantity which we relate to the elastic constants so that no complication occurs in the measurement of the path length from which the velocities are derived.

Fig. 7 shows the specimen drawn approximately to scale and the deviation of the energy rays with the wave normal is indicated.

OUTLINE OF ULTRASONIC PULSE APPARATUS USED AT NATIONAL PHYSICAL LABORATORY

The velocities of the various modes of vibration are measured by attaching two quartz crystals on opposite faces of the specimens. The quartz crystals used are either *X*-cut or *AT*-cut for longitudinal or transverse waves respectively. Short pulses ($0{\cdot}75\,\mu$s) with a carrier frequency between 5–20 Mc/s are transmitted from one face to the other at a repetition frequency of 1000 c/s. The phase of the radio-frequency pulse is synchronous with the repetition frequency in order that a steady pattern of the radio-frequency pulse may be seen on the oscilloscope tube (Fig. 8).

The received pulses are amplified by a wide band amplifier having a bandwidth of 22 Mc/s and a gain of 80 dB, and displayed on a cathode-ray tube. The time base of this tube has a duration of 2·5 μs and may be viewed through a microscope. The time base which is synchronized with the transmitter repetition frequency is delayed by a crystal controlled circuit in steps of 1 μs up to 78 μs and a further delay circuit may be set in steps of 0·001 μs. The arrival time of any pulse may be measured by setting the delay circuits to bring the image of the pulse to coincide with the cross wires of the microscope. A block diagram is shown in Fig. 9.

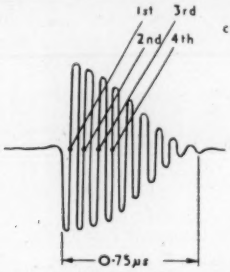

Fig. 8. Typical wave-form of ultrasonic pulse

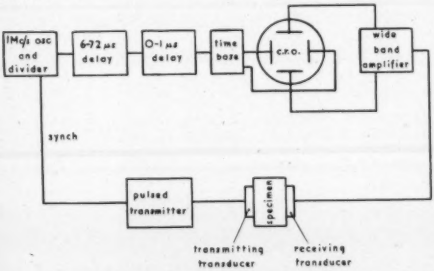

Fig. 9. Block diagram of pulse equipment

The travel times of the pulses in the specimens are deduced from the relative arrival times of the first received pulse and the successive echoes which are received in multiples of twice the travel time.

In order to reduce observational error the arrival times of the first four crossovers, Fig. 8, are recorded on each pulse. The travel times are calculated from the best fitting linear relationship between the arrival time and echo number so that the sum of the squares of the deviations from the linear relation is a minimum. Under good conditions the travel time is deduced with a standard deviation of about 1 part in 10 000.

EFFECT OF ERRORS IN X-RAY ORIENTATION MEASUREMENTS

The method described in the last section is capable in good conditions of determining wave velocities with a very high sensitivity. Unfortunately, full use of this sensitivity cannot be made when the calculation of the elastic constants depends on the knowledge of the orientation, unless this is known with sufficient precision.

Returning to the wave velocity equation for cubic symmetry

$$H^3 - aH^2 + c(a+b)\Sigma H - c(a+2b)\Pi = 0$$

The deviations in H due to small variations of the orientation functions Σ and Π are given by

$$\Delta H = \frac{-c[(a+b)H\Delta\Sigma - c(a+2b)\Delta\Pi]}{3H^2 - 2aH + c(a+b)\Sigma} \qquad (9)$$

If we now estimate the probable error in X-ray orientation measurements and insert the appropriate values of $\Delta\Sigma$ and $\Delta\Pi$ in equation (9), we then can estimate the probable errors in the three wave velocities due to this cause.

It has been shown that for a probable error of $\pm\frac{1}{2}°$ on the [110] direction on copper limits the accuracy to which the velocity may be measured to about 1 part in 2000.

PROPAGATION IN POLYCRYSTALLINE MATERIALS

The ultrasonic pulse method has been applied with success to polycrystalline materials. The limiting factor in this case is the grain size of the material which causes scattering of the ultrasonic pulse so that the waveform of successive echoes is impaired. When the grain size is large, it is usually necessary to reduce the frequency to reduce scattering.

Elastic constants may be measured very quickly with this method and when anisotropy exists this may be checked by comparing the transverse wave velocities along a path for two separate polarization directions.

Measurements were recently made on a number of steels of the plain carbon and alloy types of which the static moduli had previously been measured. The carrier frequency used was about 10 Mc/s. The test pieces were machined in three perpendicular directions from the rolled bars so as to provide a check on anisotropy. The path length in each direction was about 2 cm long.

The velocities shown in the appendix are the values for the three longitudinal and six transverse modes of vibration for each test piece. The transverse velocities were measured in each of the three directions; the transverse polarizations being parallel with the other possible directions of propagation. In the table, the lowest limits of error claimed are based on variation of travel time, measured length and density. In each mode, the travel time was measured at least four and usually six times and the scatter never exceeded 0·003 μs. Where greater limits of error are stated, the widened limits are based on the scatter between travel times in the several modes. The z axis is the rolled axis of the original bars. x and y are two directions mutually at right angles to z.

$$G = \rho V_t^2, \qquad (10)$$

$$\sigma = \frac{R^2 - 2}{2(R^2 - 1)}, \qquad (11)$$

$$\frac{E(1-\sigma)}{(1+\sigma)(1-2\sigma)} = \rho V_l^2 \qquad (12)$$

where V_l = longitudinal velocity
V_t = transverse velocity
ρ = density
$R = \frac{V_l}{V_t}$
E = Young's modulus
G = shear modulus
σ = Poisson's ratio

The table shows good correlation between the static and

Measurement of the elastic constants of the plain carbon and alloy steels

Specification	Velocities in m/s								E and G in 10^6 lb/in^2					
	zz	xx	yy	zx	zy	xz	xy	yz	yx	ρ	E	σ	G	E Static	G Static
0·4% C steel (normalized)	5934	5923	5928	3244	3246	3236	3237	3239	3236	7·828 ±0·001	30·66 ±0·07	0·287	11·91 ±0·04	30·0	11·8
0·4% C steel (spheriodized)	5932	5930	5928	3250	3250	3250	3250	3247	3247	7·838 ±0·001	30·84 ±0·03	0·286	12·00 ±0·02	30·1	11·8
0·9% C steel (pearlite)	5943	5928	5933	3216	3216	3218	3210	3216	3205	7·826 ±0·001	30·28 ±0·07	0·292	11·72 ±0·05	29·3	11·4
3% Ni steel (30/35 ton)	5868	5866	5861	3195	3195	3195	3196	3194	3196	7·837 ±0·001	29·90 ±0·05	0·289	11·60 ±0·02	29·2	11·5
3/3¼% Ni steel (45/50 ton)	5858	5854	5856	3185	3185	3183	3186	3183	3185	7·840 ±0·001	29·74 ±0·03	0·290	11·53 ±0·02	29·2	11·4
Cr Va steel (45/50 ton)	5962	5945	5957	3258	3259	3254	3252	3257	3252	7·816 ±0·001	30·92 ±0·07	0·287	12·01 ±0·03	30·3	12·1
3% Ni Cr steel (normal impact)	5855	5850	5840	3182	3182	3182	3182	3179	3180	7·825 ±0·001	29·62 ±0·07	0·290	11·48 ±0·02	29·0	11·4
3¼% Ni Cr steel (low impact)	5857	5855	5847	3181	3181	3181	3181	3181	3181	7·829 ±0·001	28·64 ±0·07	0·290	11·49 ±0·02	28·9	11·5
Ni Cr Mo steel (75/80 ton)	5870	5862	5859	3194	3194	3189	3189	3190	3190	7·820 ±0·001	29·78 ±0·07	0·290	11·55 ±0·02	29·2	11·6
Ni Cr steel (95/105 ton)	5853	5852	5851	3184	3184	3180	3180	3177	3177	7·821 ±0·001	29·60 ±0·03	0·290	11·47 ±0·03	30·0	11·3

ultrasonic values within the standard of accuracy claimable for the static measurements. However, there does seem to be a trend for the static values to be slightly lower, especially the E values.

It will also be seen from the table that the degree of anisotropy in the test pieces is quite small as the variation in velocity from one direction to another is in most cases insignificant.

CONCLUSION

Measurement of elastic constants of single crystals is carried out with very high precision by the ultrasonic pulse method. The method is entirely non-destructive and therefore observations may be repeated at any time if a check should be required. The time taken to make a set of measurements on a specimen is not long once the crystal has been prepared.

The method is also useful on polycrystals especially as the short time required for observations equally applies and quick check of isotropy is readily attained.

ACKNOWLEDGEMENTS

The author wishes to acknowledge the encouragement and assistance of Mr. H. L. Cox during the course of this work, and also the loan from Mr. M. J. P. Musgrave of the diagrams from which Figs. 2, 4, 5 and 6 have been prepared by the staff of the Central Drawing Office.

The work described above has been carried out as part of the research programme of the National Physical Laboratory and this paper is published by permission of the Director.

APPENDIX

Section on propagation of plane waves in an aeolotropic medium

Coefficients in the general wave velocity equations

$$(A - \rho v_n^2)A_x + \alpha\beta A_y + \gamma\alpha A_z = 0$$
$$\alpha\beta A_x + (B - \rho v_n^2)A_y + \beta\gamma A_z = 0$$
$$\gamma\alpha A_x + \beta\gamma A y + (C - \rho v_n^2)A_z = 0$$

are

$$A = l^2c_{11} + m^2c_{66} + n^2c_{55} + 2mnc_{56} + 2nlc_{15} + 2lmc_{16} \quad (13)$$

$$B = l^2c_{66} + m^2c_{22} + n^2c_{44} + 2mnc_{24} + 2nlc_{46} + 2lmc_{26} \quad (14)$$

$$C = l^2c_{55} + m^2c_{44} + n^2c_{33} + 2mnc_{34} + 2nlc_{35} + 2lmc_{45} \quad (15)$$

$$\beta\gamma = l^2c_{56} + m^2c_{24} + n^2c_{34} + mn(c_{23} + c_{44}) + nl(c_{36} + c_{45}) + lm(c_{25} + c_{46}) \quad (16)$$

$$\gamma\alpha = l^2c_{15} + m^2c_{46} + n^2c_{35} + mn(c_{36} + c_{45}) + nl(c_{13} + c_{55}) + lm(c_{14} + c_{56}) \quad (17)$$

$$\alpha\beta = l^2c_{16} + m^2c_{26} + n^2c_{45} + mn(c_{25} + c_{46}) + nl(c_{14} + c_{56}) + lm(c_{12} + c_{66}) \quad (18)$$

Section on measurement of elastic constants by propagation in several directions without knowledge of orientation

If H_1, H_2, H_3 are the roots of the velocity equation

$$H^3 - aH^2 + c(a + b)\Sigma H - c^2(a + 2b)\Pi = 0$$

where $H = \rho v_n^2 - c_{44}$

$$a = c_{11} - c_{44}$$
$$b = c_{12} + c_{44}$$
$$c = c_{11} - c_{12} - 2c_{44}$$
$$\Sigma = m^2n^2 + n^2l^2 + l^2m^2$$
$$\Pi = l^2m^2n^2$$

it follows that

$$a = H_1 + H_2 + H_3 \tag{19}$$

$$c(a+b)\Sigma = H_2H_3 + H_3H_1 + H_1H_2 \tag{20}$$

$$c^2(a+2b)\Pi = H_1H_2H_3 \tag{21}$$

If for the directions (a, b, c, d, e) as in Fig. 3 we designate the appropriate values of Σ and Π by Σ_a and Π_a, etc., it can be shown that

$$\Sigma_b + \Sigma_c + \Sigma_d + \Sigma_e = \frac{3}{2}\Sigma_a + \frac{1}{2} \tag{22}$$

$$\Pi_b + \Pi_c + \Pi_d + \Pi_e + \frac{5}{4}\Pi_a = \frac{1}{4}a \tag{23}$$

Now if $[H_1 + H_2 + H_3]_{a,b,c,d,e} = A_a = A_b = A_c = A_d = A_e$

$$= \text{a constant independent of orientation} \tag{24}$$

$$[H_2H_3 + H_3H_1 + H_1H_2]_{a,b,c,d,e} = B_a, B_b, B_c, B_d, B_e \tag{25}$$

$$[H_1H_2H_3]_{a,b,c,d,e} = C_a, C_b, C_c, C_d, C_e \tag{26}$$

we obtain the equations

$$A_a = a \tag{27}$$

$$B_b + B_c + B_d + B_e - \frac{3}{2}B_a = \frac{c(a+b)}{2} \tag{28}$$

$$C_b + C_c + C_d + C_e + \frac{5}{4}C_a = \frac{c^2(a+2b)}{4}\Sigma_a \tag{29}$$

An outline of the computation necessary for the determination of the three elastic constants is as follows.

First, assume a value for c_{44}, then with the velocity measurements, the various values of H may be deduced for all directions. $(c_{11} - c_{44})$ can now be found from equation (27) and hence c_{11}. The values of c_{11} and c_{44} so found are used in equation (28) to find c_{12}. A check is now applied by calculating Σ_a from equation (29) and comparing this value with that obtained from equation (20) for the a direction. The process is now repeated until by successive approximation the assumed value of c_{44} and hence c_{11} and c_{12} are so modified as to yield a value of Σ_a which satisfies equations (20) and (29) simultaneously.

From such a set of constants, the other orientation functions may be found and hence the normal to each pair of faces defined.

Commenting on the above paper **Dr. N. B. Terry** (Mining Research Establishment, Isleworth, Middlesex) said: I should like to emphasize the importance of the influence of the lateral boundaries of the specimen on the transit time of an elastic pulse traversing the specimen. For a cylindrical specimen, for example, it is well known that for certain frequencies, the velocity is a strong function of a/λ, where a is the radius of the specimen and λ the wavelength. For a thin rod, where $a/\lambda \to 0$ most of the energy is transmitted at a velocity given by $v_E = \sqrt{(E/\rho)}$, where E is Young's modulus. Although experiments by Kolsky indicate that even for thin rods some energy is always transmitted at the bulk velocity $v_B = \sqrt{\frac{E}{\rho}\frac{(1-\sigma)}{(1+\sigma)(1-2\sigma)}}$ where σ is the Poisson's ratio, it is considered that extremely sensitive apparatus is required to detect this and that for practical measurements of elastic constants the energy detected has travelled at the Young's modulus velocity. As a/λ is increased, the velocity falls, approaching that of Rayleigh surface waves for values of a/λ about 0·8. Bancroft[5] has given numerical solutions to the Pochhammer–Chree equations which show the exact dependence of velocity on a/λ for different values of Poisson's ratio. Recent measurements by Tu, Brennan and Sauer[6] have shown that if a/λ is still further increased, the pulse velocity also increases, approaching the bulk velocity for values of a/λ greater than about 2·5.

For materials of high attenuation, only pulses of comparatively low carrier frequencies may be used, and except for specimens in the form of thin rods, it is difficult to relate precisely the measured transit times to the elastic constants of the material if $a/\lambda < 2{\cdot}5$. This sets a limitation on the use of the ultrasonic pulse method for measuring elastic constants.

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The testing of fibres and their molecular structure

By P. T. Barrett, M.A., B.Sc., Ph.D., Imperial Chemical Industries Ltd., Fibres Division, Harrogate, Yorks.

In a general survey of fibre physics advancement in the understanding of the mechanical behaviour of fibres is discussed in the light of recent improvements in techniques for determining the molecular structure of fibres. The introduction of some general aspects of molecular structure is followed by detailed descriptions of new methods of measuring molecular orientation in fibres. The results of dynamic methods of measuring glass-rubber transition temperatures are described and related to the molecular orientation and mechanical behaviour of fibres at various temperatures. Elementary molecular models are introduced to explain certain aspects of the mechanical behaviour of fibres.

INTRODUCTION

One of the aims of current textile research is an understanding of the relationships in the series: molecular structure, fibre structure, fibre properties and ultimate fabric properties; in short, a unified theory of fibre properties and behaviour.

In this paper I shall be dealing with the problems of elucidating the molecular structure of fibres, and by the expression "molecular structure" I mean the configurations and movements of the molecules within the fibre. But in any case, I shall begin by explaining some of the terms used by the fibre scientist, before discussing the physics of some new methods of determining molecular structure, and I shall end by relating the results obtained to some mechanical properties of fibres.

MOLECULAR STRUCTURE

The molecules of textile fibres are distinguished by their length. Generally the length to breadth ratio for a molecule may be four or five, but this ratio for the molecule of a textile fibre runs into the order of hundreds. This is a feature which contributes to the high tensile strength of a single filament, for it is found that the long molecules lie roughly parallel to the filament axis and are locked in this position by chemical cross links or crystallinity. In a synthetic fibre this axial orientation of molecules is induced by extending or drawing the fibre during the later stages of the manufacturing process, the first stage of which consists of extrusion into continuous filaments from a melt or solution of the high polymer.

The long chain synthetic fibre molecule is built up from a large number of identical segments, each segment being a much simpler molecule which is characteristic of the material and is known as the monomer or repeat unit. Fig. 1 shows

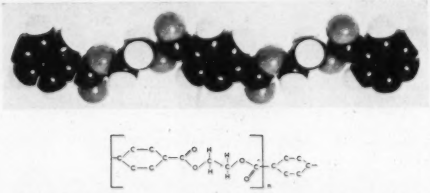

Fig. 1. Molecular model of polyethylene terephthalate (repeat unit $-CO.O.C_6H_4.O.CO.(CH_2)_2-$)

two such repeat units for the polyethylene terephthalate molecule $C_6H_4.CO.O.(CH_2)_2.O.CO$ which is the polyester from which Terylene fibre is made. The segment addition processes during manufacture may not be quite so regular as I have indicated. For example, branching of the polymer molecule may occur and, where asymmetry is present, head to tail addition may be mixed with head to head addition, etc. These various types of structure give rise to a variety of properties in the final material.

Most useful textile fibres have regions of crystallinity in them which are very small in size compared with the filament diameter. The ability of a long chain polymer molecule to crystallize depends, among other things, upon the symmetry of the molecular repeat units along its length. Branching of the chain and asymmetry in the disposition of the repeat units along the chain length both reduce the ability of the polymer to crystallize.

The ratios of crystalline to amorphous material may be roughly deduced from measurements of density, if the densities of the amorphous and wholly crystalline states are known. The crystalline-amorphous ratio may also be deduced from intensity ratios of the X-ray diffraction patterns from each phase of the material. Finally, several polymers show a modified infra-red absorption spectrum when the material under examination is crystalline and the extent of the modification may be taken as a measure of the crystalline-amorphous ratio in selected instances.

MOLECULAR ORIENTATION

I now want to discuss the subject of molecular orientation. In the amorphous phase, the preferred state of a collection of long molecules is one of complete disorder. However, the processing of long chain polymer molecules into fibres involves extrusion through a die, being stretched while solidifying or coagulating, and possibly a further stretching processing whilst the material is in the solid state. The severe tensile stresses which the material undergoes have the result of alining the polymer molecules with a preferred axial orientation and this results in an improvement in axial strength. In much the same way as it is easier to pull apart two pieces of sticky tape by forces applied at right angles to their length, than it is by forces applied parallel to their length, so molecular segments lying across the fibre axis flow past each other more readily than do molecular segments lying parallel to the fibre axis. Fig. 2 shows in diagrammatic form the several microphysical states of fibre material which are thought to exist.

The extent of this preferred axial orientation and its division between the crystalline and amorphous phases is both of fundamental and of practical importance. For example, the thermal crystallization of a randomly oriented high polymer may be described thermodynamically by the product of two rate processes; *viz.* nucleation and crystal growth, which together give rise to a maximum in the rate of crystallization versus temperature curve at some temperature below the

melting point. When the mutual alinement of molecules is improved, however, by overall axial orientation, both the rates of nucleation and crystal growth are increased by orders of magnitude.

A measure of the overall preferred orientation is given by the strength of birefringence, which is simply the difference between the refractive indices of the filament for light polarized parallel and perpendicular to the filament axis. The birefringence will be a maximum for a filament with all its molecules alined parallel to the axis.

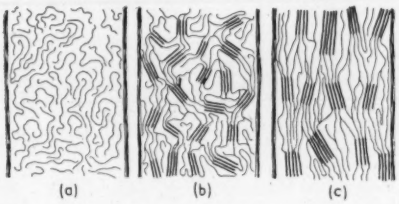

Fig. 2. Schematic representation of an amorphous polymer (*a*), a crystalline polymer (*b*), and an oriented crystalline polymer (*c*)

The direct method of measuring the birefringence of a filament by determining the refractive indices separately for light polarized parallel and perpendicular to the axis can be done by immersing the filament in a series of liquids of different refractive indices until the outline of the filament disappears, when an exact refractive index match has been made; but this method is rather tedious.

It is more usual to measure filament birefringence by using light polarized at 45° to the axis of the filament and a quartz or calcite compensator to determine the relative retardation (i.e. path length × birefringence along that path) at the centre of the filaments. Incident light polarized at 45° to the axis of the filament may be considered to be the result of two component vibrations of equal amplitude and in phase, one vibration along the axis and the other across the axis. On emerging from the centre of the filament, these component vibrations will be out of phase by δ radians depending upon the birefringence Δ, the filament diameter d and the wavelength of the light used, where:

$$\frac{\delta}{2\pi} = \frac{\Delta \,.\, d}{\lambda} = \frac{\text{optical relative retardation}}{\lambda}$$

The quartz or Babinet compensator consists of two birefringent quartz wedges as shown in Fig. 3. When inserted into the optical system, the fixed wedge A has the effect of adding a certain amount of optical relative retardation in the direction OY; the movable wedge adds relative retardation in the direction OX. When placed between crossed Nicol prisms or polaroids the Babinet compensator produces in the field of view a set of straight-line fringes separated by a distance equivalent to one wavelength of relative retardation. If a birefringent filament of circular cross-section is inserted in the field of view, the fringes are displaced as shown and the ratio of the displacement to the fringe spacing is equal to $\Delta \,.\, d/\lambda$, thereby enabling the birefringence to be measured. Some idea of the difficulty in estimating this fringe shift may be gained from Fig. 4, and in fact the method is prone to large subjective errors. A similar principle is employed with the Berek compensator, but here a variable optical path and degree of compensation is obtained by tilting a plate of calcite.

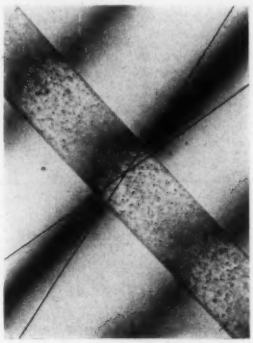

Fig. 4. A typical Babinet fringe

Two new methods of measuring birefringence have been devised within Fibres Division of Imperial Chemical Industries Ltd., both of which are intrinsically more accurate than the established methods since they are immune from operator errors. I will now describe the physics of the principles upon which these new methods are based. The centre of a birefringent filament whose axis is inclined at 45° to the plane of polarization between Nicol prisms will transmit elliptically polarized light to the analysing Nicol as shown in Fig. 5. The plane polarized light incident upon the filament may conveniently be regarded as being the result of the two in-phase vibrations of equal amplitude parallel to the OX and

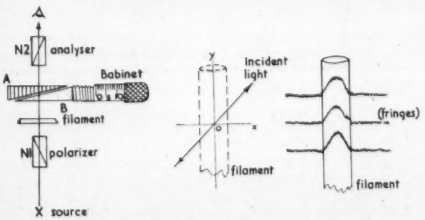

Fig. 3. Arrangement of the Babinet compensator system of measuring birefringence

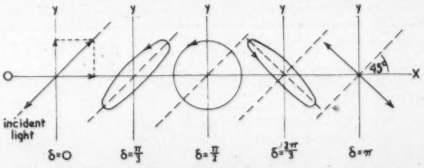

Fig. 5. Composition at right angles of two simple periodic motions of the same frequency and amplitude but different phase

OY axes. On travelling through the centre of the filament the OY vibration will suffer a retardation in phase relative to the OX vibration given by the expression $\delta = 2\pi\Delta d/\lambda$. The magnitude of this phase retardation determines the degree of ellipticity of the light transmitted to the analysing Nicol and analysis shows that the major and minor axes of the ellipse always lie along the 45° lines.

In the first method the birefringent filaments are simply mounted in a flat ribbon in air at 45° to the plane of polarization between crossed Nicol prisms, when the intensity of the light transmitted by the analysing Nicol will be a function of the filament diameter, the opacity of the material, the optical retardation and the wavelength of the light used. The form of this function can either be calculated or derived by experiment and it is them possible in principle to use this as a basis for the measurement of optical retardations. The theoretical problem is to calculate the intensity of light transmitted by a filament of given opacity, diameter and birefringence. It is complicated by the occurrence of light scattering within the filament and by optical reflection and refraction at the surface of the filament. Neglecting these two phenomena, however, the calculated function has the form shown by the full curve in Fig. 6, wherein the practical limit of the method is seen to lie at a phase change of π radians.

There are two points of special interest in this method; one is the fact that by virtue of being mounted in air, the filaments act as cylindrical lenses of very short focal length exhibiting a high degree of aberration. In practice then, only the rays of light passing through the centre of the filament contribute to the transmitted intensity and this produces the broken curve shown in Fig. 6 of the form

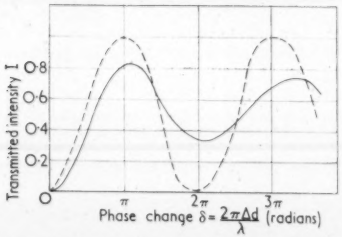

Fig. 6. The intensity of light transmitted by a birefringent filament when placed between crossed Nicol prisms

$$I = Nkd\,[1 - \int_0^{\pi/2} \cos(2\pi\Delta d \sin\theta/\lambda) \sin\theta\, d\theta]$$

where I = transmitted intensity
N = number of filaments
k = a constant
λ = wavelength of light used
d = filament diameter
Δ = birefringence of filament.

$(1 - \cos\delta)$, since we are now dealing with a filament of effectively rectangular cross-section. The other point of interest is that diffraction effects which occur at the edges of the filament, can safely be ignored for the diffracted light remains plane polarized and is stopped by the analysing Nicol in the crossed position.

The second new method of measuring birefringence rests upon two facts, the first of which is that the major and minor axes of the elliptically polarized light emerging from the centre of the filament always coincide with the 45° lines. The second fact is that the ellipse can be reconstructed from two vibrations of unequal amplitude along the 45° lines, $\frac{1}{2}\pi$ out of phase. As the relative phase retardation of the filament alters, only the relative amplitude of these subsidiary vector vibrations will be affected, their phase difference will remain at $\frac{1}{2}\pi$.

If now this elliptically polarized light is passed through a quarter-wave plate which retards one vibration relative to the other by a phase angle equal to $\frac{1}{2}\pi$, the in-phase addition of these vectors produces plane polarized light again, oriented at some angle ϕ to the original plane of polarization, where $\phi = \frac{1}{2}\delta = \pi\Delta d/\lambda$.

As described, this method is a classical microscopic one attributed to Sénarmont.[1] With the axes of the quarter-wave plate parallel and perpendicular to the plane of polarization, the analysing Nicol is rotated until the field of view is completely dark; this is the reference extinction angle. The filament is now mounted between the polarizing Nicol and the quarter-wave plate so that its axis is at 45° to the plane of polarization. The analysing Nicol is then rotated to a new position where the centre of the filament is completely dark; this angular displacement is equal to half the phase retardation introduced across the centre of the filament. The microscopic method when applied to filaments is tedious and difficult, since the operator is endeavouring to "extinguish" the centre of the filament against a background, the intensity of which is varying with the position of the analysing Nicol. The microscope objective too is never strain-free and exhibits birefringence effects.

The novel feature of our method is that of analysing only the light scattered through the filaments which are mounted in air in the absence of lenses, as shown in Fig. 7. In this

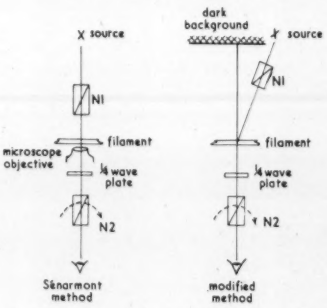

Fig. 7. Arrangements of the Sénarmont and modified methods of measuring birefringence

manner the filaments under examination are viewed against a uniformly dark background, thereby improving the accuracy of the method and enabling the intensity of scattered light transmitted by the analysing Nicol to be monitored photoelectrically as shown in Fig. 8 of the complete birefringence instrument. The scattering angle is chosen to be as small as practicable in view of the extraneous polarization due to scattering, together with the severe loss of intensity at larger angles. As in the previous method, only the light passing through the centre of the filament is analysed, and all the

diffracted light is contained in the forward beam. By virtue of the optical nature of the test and by mounting and examining the filaments in air, these new methods of measuring birefringence are intrinsically non-destructive.

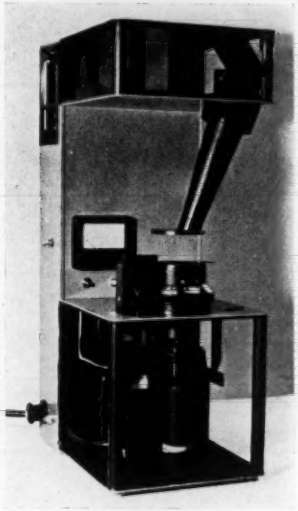

Fig. 8. An instrument for measuring birefringence

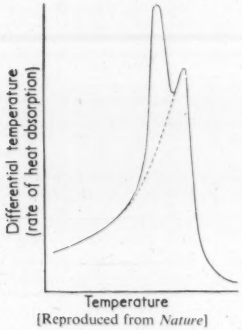

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Fig. 9. Differential heating curves for melting 6·6 nylon fibres; - - - - - undrawn yarn; ——— drawn yarn

The birefringence is a measure of the total (i.e. amorphous plus crystalline) orientation in a fibre. The amount of orientation present in the amorphous phase can be measured, even in partially crystalline fibres, by means of dichroic ratios, which are simply the ratio of the absorption coefficients for light polarized parallel and perpendicular to the axis of a filament which has been suitably dyed. The dye penetrates the amorphous regions only, assumes the orientation of the amorphous material, and is itself dichroic, that is to say it has different absorption coefficients for light polarized parallel and perpendicular to its crystal axis.

An apparatus has been developed within the Fibres Division of Imperial Chemical Industries Ltd. in which a magnified image of the dyed filament is projected on a narrow slit in front of a photomultiplier and the filament is traversed by means of a mechanical stage so that the intensity of light transmitted by the centre of the filament can be measured for light polarized parallel and perpendicular to the axis of the filament.

Estimates of crystalline orientation may be obtained from X-ray data. An alternative method has been proposed by White[2] who measured the rate of heat absorption for a bundle of nylon fibres versus temperature up to the melting point as shown in Fig. 9. His results suggest that the large absorption peak below the melting point is due to the disorientation of the oriented crystallites.

SECOND-ORDER TRANSITION TEMPERATURES

Before discussing a few aspects of the mechanical properties of fibres, I want to mention second-order transition phenomena in synthetic high polymers. We are familiar with the abrupt change in properties which occurs on the melting of a crystalline material. Now, in addition to a crystalline melting point, synthetic high polymers generally possess a narrow temperature range over which a similar change of properties occurs on a reduced scale. For example, there is a rapid fall in initial modulus for acetate rayon[4] at its second-order transition temperature of 180° C, and amorphous Terylene polyester fibre shows a decay of birefringence at 70° C. These temperatures may be thought of crudely as amorphous melting points, for below them the polymer is a hard glass-like substance and above them the material is pliable and rubber-like. They have been given the names of apparent second-order transition temperatures, or glass-rubber transition temperatures.

Current thoughts on the molecular processes responsible for glass-rubber transition temperature phenomena picture a tangled skein of long chain polymer molecules locked in an amorphous structure, unable to yield to an applied stress and behaving in a glass-like manner. At the glass-rubber transition temperature certain molecular segments are thought to possess sufficient thermal energy to revolve, so that under an applied stress these segments will be able to wriggle past each other and the material will yield in a rubber-like manner.

Another effect which follows from what has been said above is that there is a sharp rise in the energy absorption of the high polymer subjected to cyclic strains at the glass-rubber transition temperature. For example, if a bundle of fibres is held between clamps and then stretched and relaxed at a particular frequency, then the amount of work required to stretch the fibres will be more than the amount of work done by the fibres in the recovery half of the cycle. The amount of hysteresis energy lost is dissipated as heat and the ratio of this to the total work done in stretching is called the specific loss of the material for that particular frequency and temperature. A typical loss curve versus temperature for Terylene polyester fibre is shown in Fig. 10, where the effect of microphysical structure on the molecular process responsible for the losses is illustrated. It will be noticed that the loss peak corresponding to the glass-rubber transition temperature is flattened and moved to a higher temperature

for each increase in the internal order of the system. This ends my discussion on the molecular structure of fibres and now in conclusion I want to use some of these ideas in explaining and correlating a few aspects of the mechanical properties of fibres.

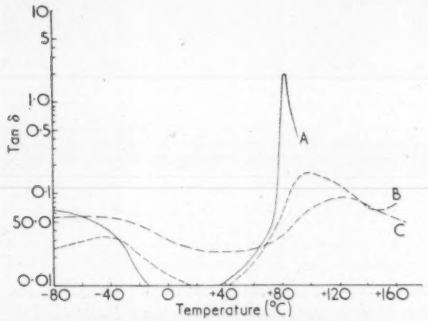


Fig. 10. Typical hysteresis loss curve against temperature for polyethylene terephthalate

A, amorphous unoriented; *B*, crystalline unoriented; *C*, crystalline oriented.

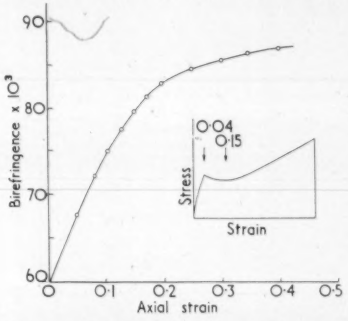


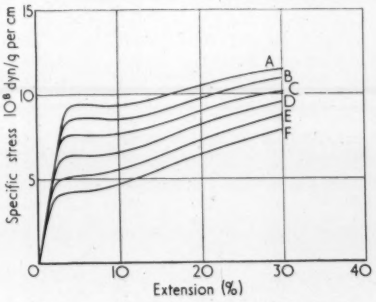
Fig. 11. Birefringence as a function of axial strain for a Terylene monofilament of draw ratio 3·5/1

MECHANICAL PROPERTIES OF FIBRES

The strong time dependence of stress and strain exhibited by high polymeric fibres must enter into any discussion on the micro-physical and molecular mechanisms governing the response of fibres to applied stresses. For any given rate of strain, the measured stress in a stress/strain diagram will be a reflexion of the stiffness of the molecular mechanisms on an increasing scale of response times. For example, apart from the very stiff mechanisms of bond stretching and bending, the fastest responding molecular mechanism which a fibre possesses is that of chain uncoiling, which is achieved by bond rotation. Uncoiling mechanisms are thought to be responsible for very nearly the whole of the initial straight Hookean part of a stress/strain curve as is suggested by Fig. 11 showing the increase of birefringence with strain.

Extensions greater than the yield strain are accomplished by further uncoiling and the irrecoverable flow of polymer chains past each other, which can take place only when neighbouring segments have been moved aside laterally against the viscosity of the system. If the temperature is altered, the effective viscosity of the system will change and the difference in the response times of the molecular uncoiling and flow mechanisms will be reflected in the stress/strain curves. Similarly the response of these mechanisms will depend upon the frequency of testing in cyclic work, or the rate of extension in "static" testing[3] as shown in Fig. 12. More generally still, there is a direct relationship in dynamic testing between the strain frequency and the temperature for any particular polymer under certain conditions. For amorphous Terylene polyester fibre at room temperature, a change in frequency by a factor of 10 is equivalent to about 3° C of temperature.

Returning to the Hookean portion of the stress/strain curve, let us consider the effects of orientation and crystallinity upon the initial modulus of a fibre. Segments of molecules which lie at an angle to the fibre axis can rotate about a primary bond and make a contribution to the elongation of the fibre. In performing this rotation they are helped, of course, by the applied stretching force and by whatever thermal energy they happen to possess at that instant. Molecular segments which lie parallel to the fibre axis can contribute to the tensile strain by means of bond bending and opening of valency angles, a far stiffer mechanism than that of bond rotation. It follows then from these crude arguments that the initial modulus increases with increasing molecular axial orientation and hence with birefringence. When the fibre is crystallized, the stiffness of the whole molecular environment is increased and this enhanced resistance to molecular movement is reflected in greater values of initial modulus and of torsional modulus.



[Reproduced from *Journal of the Textile Institute*]

Fig. 12. Curves for cellulose acetate rayon at rates of extension from 0·0013 to 1096% per second

A, 1096; *B*, 269; *C*, 22; *D*, 2.0; *E*, 0.08; *F*, 0.0013.

The molecules within a crystallite are rigidly bound and relative molecular movement is impossible, so that although the presence of crystallites can increase the stiffness of the whole structure, the molecular movements which give rise to the overall fibre strain occur in the amorphous regions of the

fibre. It follows then that it is the molecular orientation in the amorphous regions of the fibre which largely control the initial modulus. For example, drawn fibres of Terylene polyester fibre have an initial modulus of 120 g./denier and this falls to a value of 60 g/denier when the dichroic ratio shows that the amorphous orientation has been reduced by shrinkage in boiling water.

Finally, a word about the effects associated with the glass-rubber transition temperature. At this temperature you will remember, the amorphous phase "melts" and the glass-like properties, which the fibre exhibited below this temperature are replaced by rubber-like properties above it and this is reflected in a sharp fall in the values for initial modulus.

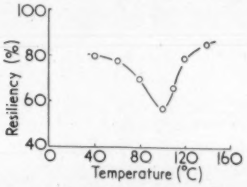


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Fig. 13. Resiliency-temperature behaviour of Dynel

Crystalline regions in fibres are unaffected by the glass-rubber transition of the amorphous material, so that the fall in initial modulus through the glass-rubber transition temperature range is much less marked for partially crystalline materials.[4]

Fig. 13[4] shows the minimum in the length recovery (or resiliency) curves at the glass-rubber transition temperature for a partially crystalline material. At this temperature we think that some molecular segments assume an ability to rotate. If this is so, they will absorb mechanical energy on the loading half of the cycle, leaving less energy to be released on unloading, so that the material exhibits a peak in its dynamic loss curve and also reduced recovery characteristics. Above the glass-rubber transition temperature the rotating segments can derive sufficient energy from pure thermal vibrations and less energy is absorbed from an imposed mechanical strain so that the recovery properties are improved, at least in partially crystalline materials which do not become completely fluid above this temperature. The length recovery of cellulose acetate, an amorphous material, falls to zero at the glass-rubber transition temperature.

CONCLUSION

It has been my purpose in this paper to discuss the physics of some new aspects of the non-destructive testing of fibres. For those who are not primarily interested in textiles, I hope that I have had some measure of success in making the main theme more palatable by clothing it in a general survey of fibre physics and molecular structure.

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